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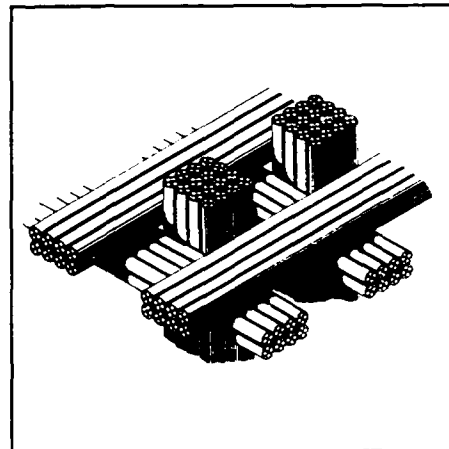
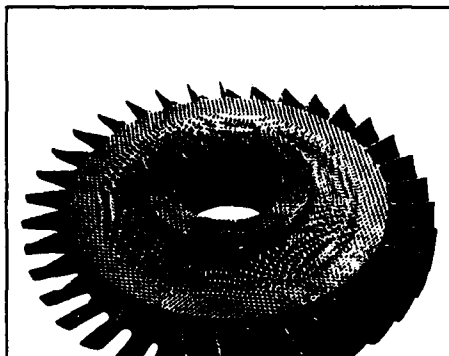
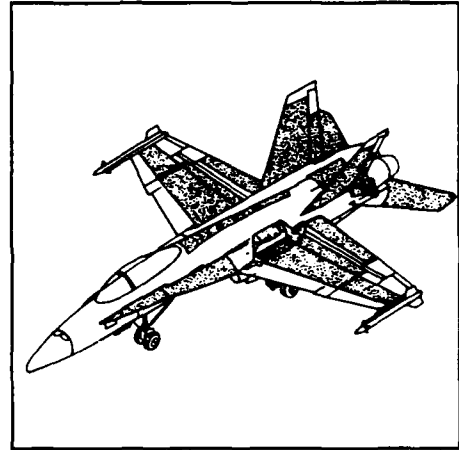
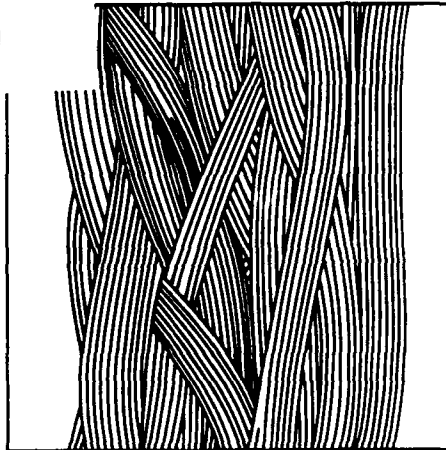
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**HIGH-PERFORMANCE**

**SYNTHETIC FIBERS**

**FOR COMPOSITES**

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This report describes the properties of the principal classes of high-performance synthetic fibers, as well as several current and potential methods of synthesis and processing to attain desirable properties. Various promising classes of materials and methods of fiber synthesis are suggested for further investigation.

Successful fiber reinforcement of a matrix is heavily dependent on the interfact between the two components. The report emphasizes our relatively poor fundamental understanding of fiber-matrix reactions and this "interphase" region. Research directed at improving our understanding of the properties and behavior of the boundary region is identified as a prime need if advances are to be made in fiber and composite performance. The report emphasizes the complex interdisciplinary nature of fiber science and makes strong policy recommendations for long-range continuity of fiber research and for increased support of education in fiber science. Because of the highly international scope of the commercial fiber and composites industries and the critical importance of fibers for military and space applications, the report considers the consequences of government policy affecting these industries. Attention is called to the need for improving procedures leading to governmental decisions affecting the fiber industry. The need for a policy to provide support for development and production of small quantities of specialty fibers for strategic military applications is also emphasized.

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# HIGH-PERFORMANCE SYNTHETIC FIBERS FOR COMPOSITES

Report of the Committee on  
High-Performance Synthetic Fibers for Composites

NATIONAL MATERIALS ADVISORY BOARD  
Commission on Engineering and Technical Systems  
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This report describes the properties of the principal classes of high-performance synthetic fibers, as well as several current and potential methods of synthesis and processing to attain desirable properties. Various promising classes of materials and methods of fiber synthesis are suggested for further investigation.

Successful fiber reinforcement of a matrix is heavily dependent on the interface between the two components. The report emphasizes our relatively poor fundamental understanding of fiber-matrix reactions and this "interphase" region. Research directed at improving our understanding of the properties and behavior of the boundary region is identified as a prime need if advances are to be made in fiber and composite performance.

The report emphasizes the complex interdisciplinary nature of fiber science and makes strong policy recommendations for long-range continuity of fiber research and for increased support of education in fiber science.

Because of the highly international scope of the commercial fiber and composites industries and the critical importance of fibers for military and space applications, the report considers the consequences of government policy affecting these industries. Attention is called to the need for improving procedures leading to governmental decisions affecting the fiber industry.

The need for a policy to provide support for development and production of small quantities of specialty fibers for strategic military applications is also emphasized.

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## PREFACE

High-performance synthetic fibers are key components of composite materials, a class of materials vital for U.S. military technology and for the civilian economy. The compositions of the fibers cover a wide range of chemical substances, including elementary carbon and boron, refractories such as inorganic carbides and oxides, and organic polymers. Fibrous forms of these materials are used to reinforce a similar range of matrix materials, and metals, producing composites with physical properties superior to those of unreinforced matrices. The emphasis in fiber research has been on the attainment of high-performance mechanical and thermal properties for structural applications, particularly for aerospace vehicles and aircraft.

The objective of this study is to survey major research and development opportunities for high-performance fibers needed for present and future structural composite applications and to identify steps that the federal government could take to accelerate the commercialization of this critical fiber technology in the United States. The report begins with background information on the fibers currently available for composite applications, their major uses, current and projected demands, costs, and sources of supply. New fibers and improvements in fiber properties that are needed for the various types of structural composites are discussed. The report then evaluates various approaches to fiber synthesis and processing that have the potential to either fulfill these needs or significantly reduce the cost of structural composites. The report also reviews ongoing research and development in areas that are of general importance to fiber science and technology (surface properties and treatments, fiber-matrix bonding, and fiber coatings and coating processes). Recommendations are made for future research that will be necessary to improve existing high-performance fibers and develop new ones. Included are specific steps that should be taken to ensure a domestic supply of existing and new high-performance fibers.

The report is concerned primarily with the reinforcing fibers needed in structural applications over the wide range of temperatures encompassed by organics, metals, and glass/ceramics. However, recognition is made of applications in which other useful physical properties of a fiber, such as electrical conductivity, thermal conductivity, magnetic or piezoelectric properties, allow the engineered structure to be dual or multipurpose.

Since high-performance fibers represent a new technology, in many cases only limited information exists. Thus, the length of the various sections in the report is not necessarily indicative of the importance of the topic covered.

Russell J. Diefendorf  
Chairman

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Speakers at the second meeting included William B. Hillig, General Electric Corporate Research and Development, who discussed potential composite systems and fibers; George F. Hurley, Los Alamos National Laboratory, who briefed the committee on whisker reinforcements; and Roger Bacon, AMOCO Performance Products, Inc., who talked about carbon fibers. Penny Azerdo, Pratt & Whitney Corporation, presented a paper on interactions in intermetallic systems; George Reynolds, MSNE, Inc., discussed interactions in ceramic systems; and committee member James Sorensen talked about interactions in high-temperature aircraft composites. Committee member Karl Prewo's presentation covered Japanese developments in fibers and committee member Ruey Y. Lin discussed chemical conversion of precursor fiber.

Presentations at the third meeting were made by Stanley Channon, consultant, who discussed a survey of world fiber production and technological capabilities; Joseph C. Jackson, SACMA, who described the comprehensive review his organization was preparing for a government presentation covering virtually all aspects of the fiber and composites industries; Greg Corman, General Electric (R&D), who talked about creep in single-crystal oxides; Ed Courtright, Battelle Pacific Northwest, who discussed oxygen permeability studies; Robert S. Feigelson, Stanford University, who discussed single-crystal preparation and properties, emphasizing the laser-heated pedestal growth technique; and Gary Tibbetts, General Motors Technology Center, who talked about carbon whiskers. These presentations proved to be valuable contributions to the technical contents of this report.

Special thanks also go to Donald E. Ellison, Donald E. Ellison & Associates, who supplied valuable input for the section on technology export and export control.

The chairman thanks the committee members for their dedication and for the patience shown during the numerous iterations and revisions of the report drafts. The liaison members are thanked for their active participation in committee discussions and for providing valuable support documents and data.

Finally, special thanks go to James H. Schulman, NMAB program officer, and Janice Prisco, project assistant, whose dedicated efforts made possible the production of this report.

# CONTENTS

|   |        |
|---|--------|
| EXECUTIVE SUMMARY, Conclusions, and Recommendations.....                                      | 1      |
| <br><b>1</b> High-Performance Synthetic Fibers for Composites.....                            | <br>9  |
| Introduction, 9   |        |
| Present Materials: An Overview, 11  |        |
| Characteristics of Materials in Fiber Form, 12  |        |
| Advances in Fiber Technology, 13  |        |
| Types of High Performance Fibers, 16  |        |
| Fiber-Reinforced Composites, 16   |        |
| References, 19  |        |
| <br><b>2</b> High-Performance Fiber Materials: Applications,<br>Needs, and Opportunities..... | <br>21 |
| Introduction, 21  |        |
| High-Performance Fibers for Polymeric Matrix Composites, 21                                   |        |
| High-Performance Fibers for Metal Matrix Composites, 29                                       |        |
| High-Performance Fibers for Ceramic Matrix Composites, 34                                     |        |
| High-Performance Fibers for Carbon-Carbon Composites, 41                                      |        |
| High-Performance Fibers for Nonstructural Applications, 43                                    |        |
| References, 47  |        |
| <br><b>3</b> Fiber-Forming Processes: Current and Potential Methods.....                      | <br>49 |
| Introduction, 49  |        |
| Processes to Form Polymeric Organic Fibers, 51  |        |
| Fiber Formation by Pyrolytic Conversion of<br>Precursor Fibers, 54                            |        |
| Silicon Carbide and Silicon Nitride Fibers, 65  |        |
| Oxide Fibers, 70  |        |
| Chemical Conversion of a Precursor Fiber (CCPF), 75   |        |
| Chemical Vapor Deposition, 79   |        |
| Technical Future, 84  |        |
| Alternative Processes, 88   |        |
| Fiber Coatings, 90  |        |
| Observations and Conclusions About Fiber Fabrication<br>and Processing, 98                    |        |
| References, 98  |        |

|          |   |     |
|----------|---|-----|
| <b>4</b> | Important Issues in Fiber Science/Technology.....                 | 103 |
|          | Introduction: Overview of Needed Research and<br>Development, 103 |     |
|          | Summary of Technical Issues, 106                                  |     |
|          | References, 108   |     |
| <b>5</b> | Important Policy Issues.....                                      | 109 |
|          | Introduction, 109   |     |
|          | Education in Fiber Science and Technology, 110                    |     |
|          | Domestic Sourcing Considerations, 111                             |     |
|          | Technology Export/Export Control, 113                             |     |
|          | Production of Small Quantities of Specialty Fibers, 114           |     |
|          | Foreign Competition, 115  |     |
|          | Continuity of Support, 116  |     |
|          | Glossary of Terms.....  | 119 |
|          | Appendix.....   | 127 |

## TABLES AND FIGURES

|            |  |
|------------|--|
| TABLE 1.1  | High Performance Fibers, 10  |
| TABLE 1.2  | Properties of polyamid in various forms, 12                                      |
| TABLE 2.1  | Advantages of PMCs, 22   |
| TABLE 2.2  | Advantage of PMCs, 29  |
| TABLE 2.3  | Low-cost (aluminum-matrix) MMCs for Industrial and aerospace applications, 31    |
| TABLE 2.4  | Some higher-cost MMC aerospace applications, 31                                  |
| TABLE 2.5  | Some current high-performance-fiber reinforced MMC systems under development, 33 |
| TABLE 2.6  | Commercially available fibers for the reinforcement of CMCs, 35                  |
| TABLE 2.7  | Manufacturing process for CMCs, 38   |
| TABLE 2.8  | Some applications of CMCs, 39  |
| TABLE 2.9  | Some current sources of CMCs, 40   |
| TABLE 2.10 | Major uses of C-C composites, 42   |
| TABLE 3.1  | Carbon fiber classification, 58  |
| TABLE 3.2  | Oxide fibers, 71   |
| TABLE 3.3  | Refractory fibers prepared by chemical conversion of a precursor fiber, 76       |
| TABLE 3.4  | Comparative properties of reinforcing fibers, 81                                 |
| TABLE 3.5  | Materials produced by CVD processes, 94  |

- FIGURE 1.1 Maximum-use temperatures of various structural materials, 11
- FIGURE 1.2 Strength of typical commercial organic fibers, 14
- FIGURE 1.3 Fiber price versus bundle size and fiber physical properties, 15
- Figure 1.4 Specific strength and modulus of high-performance fibers and other materials "specific property" means the property divided by the density, 16
- FIGURE 2.1 U.S. carbon fibers consumption by major market segment, 24
- FIGURE 2.2 U.S. carbon fiber consumption aerospace market, 24
- FIGURE 2.3 Comparison of bend tests for unreinforced cement and cement-matrix composites containing 2 percent chopped carbon fiber, 36
- FIGURE 2.4 Densities and use temperatures of potential composite matrices, 37
- FIGURE 2.5 Specific strength comparison of high-temperature metal alloys and advanced composites (two-dimensional fiber-matrix), 39
- FIGURE 3.1 General processing steps for converting high bulk materials to fibers, 50
- FIGURE 3.2 Simplified flowsheet for precursor pyrolysis processes, 55
- FIGURE 3.3 PAN Based Process, 57
- FIGURE 3.4 Pitch based process, 62
- FIGURE 3.5 Production of Si ceramic fibers from polymetric precursors, 67
- FIGURE 3.6 Variation of tensile strength with flaw size, 68
- FIGURE 3.7 Scanning electron micrograph of fracture surface of mullite fiber, 74
- FIGURE 3.8 Transmission electron micrograph of ion milled section of mullite fiber, 74
- FIGURE 3.9 SEM of fiber FP surface, 74
- FIGURE 3.10 SEM of PRD-166 surface, 74

- FIGURE 3.11 Boron filament reactor, 82
- FIGURE 3.12 Photomicrographics of boron fiber, 82
- FIGURE 3.13 Histogram of boron fiber tensile strength, 82
- FIGURE 3.14 Histogram of CVD SiC fiber tensile strength, 82
- FIGURE 3.15 Schematic drawing of the  $\mu$ -cz technique, 87
- FIGURE 3.16 Description of the production of vapour-grown fibres, 87
- FIGURE 3.17 Illustration of the VLS process for SiC whisker growth, 89
- FIGURE 3.18 A schematic diagram of the pedestal growth method, 89
- FIGURE 3.19 Schematic view of a continuous fiber electroplating process, 91
- FIGURE 3.20 Schematic diagram of the CVE process, 93
- FIGURE 3.21 Schematic of a continuous CVD fiber-coating line, 94
- FIGURE 3.22 Metallorganic deposition process, 95
- FIGURE 4.1 Structure and composition of SiC fiber produced by chemical vapor deposition, 107
- FIGURE 4.2 Interphase region produced during fabrication of Nicalon fiber reinforced glass-ceramics, 107
- FIGURE 4.3 Fracture surface of boron reinforced 6061 aluminum with prenotched region also shown, 107
- FIGURE 4.4 Fracture surface of Borsic reinforced titanium with prenotched region also shown, 107



## **EXECUTIVE SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS**

High-performance fibers are unique because they are an enabling technology for so many present and future high-technology products. If the United States is to remain a leader in technology-based products, support for the development of these new fibers is vital. Loss of leadership in the production of these fibers could lead to the loss of our international dominance in aircraft production and further weaken our competitiveness in the automotive market. Indeed, loss of our leadership role in these fibers could have a markedly deleterious effect on the U.S. economy.

The strengthening of materials by incorporating fibers as the primary load-bearing or fracture-inhibiting components in otherwise weak matrices occurs in nature (e.g., wood, bone). Man has made use of this principle since ancient times (e.g., in making of bricks reinforced with straw). The advanced composites industry is the modern expression of this technology, wherein exceptionally strong and stiff (high-performance) organic or inorganic fibers are embedded in a variety of matrices—polymer, ceramic, or metallic—to produce lightweight products with structural properties vastly superior to those of the separate components.

Because of their low density and high strength or modulus, advanced composites have become critical components for modern aircraft and aerospace vehicles, and they play an essential role in assuring U.S. preeminence in these industries. The same characteristics have contributed to their application to other fields, from automotive components to electronics to recreation products. With lowered production costs, a vast expansion of their applications to many other areas is possible, making them of even greater economic importance.

Present defense applications put a premium on high-strength and high-temperature performance and current government-sponsored research on high-performance fibers is directed toward improving their mechanical and thermal properties either through the development of new fibers or through new methods of synthesizing or processing existing reinforcing fibers. However, improvements in these fibers (performance per dollar) can be expected to have a significant effect on civilian end products as well. Future developments, leading to cost-effective parts production driven by improved or new types of synthetic fibers, improved manufacturability, and reduction in manufacturing costs, will create entirely new practical applications for fiber-based materials (e.g., in building construction and automotive applications). The

market for a low-price, high-performance fiber could be extremely large, rivaling that of the present synthetic fiber industry. Thus, it is probable that domestically produced high-performance fibers will be every bit as vital to the economic health of the United States as they are to its security.

Industrial interest in all aspects of advanced composites, including research and development on high-performance fibers, is international. Certain aspects of U.S. industrial and government practices, particularly the short time frame and lack of continuity of research and development (R&D) support, make the American fiber industry vulnerable to the strong competition it faces from Europe and Japan.

### CONCLUSIONS AND RECOMMENDATIONS

Conclusion 1. High-performance fibers are the backbone of the advanced composites industry, which is a critical U.S. industry because of its strategic defense applications and its role in the creation of new products for the domestic and international markets. The United States is in danger of losing its preeminent position in this industry unless steps are taken to strengthen the technology, facilitate its implementation, and broaden the industrial base for high-performance fibers.

Because advanced fibers are of such long-term importance to our national security and economy, they require long-range programs to develop sound technical principles and continuing substantive technical progress. However, some of the federal government's major systems development programs, whose ultimate success depends on advanced composites, are attempting to schedule the creation and optimization of advanced fibers on an inappropriate engineering time schedule.

Recommendations. Government and industry should each address the problem of maintaining fiber R&D as a continuous, uninterrupted activity and should establish appropriate means for funding this mode of fiber development. Government-funded development of high-performance fibers should not be relegated to a subtask of a systems development project with an engineering time schedule.

Closer and more frequent communication on issues of technology, development, and supply should be established between the government, private companies, trade associations, and universities.

Conclusion 2. High-performance fiber development has been guided mainly by aerospace application demands for lighter, stronger, stiffer, and higher-temperature fibers. These goals, rather than low cost, have been the primary factors dictating the choice of manufacturing processes. There are, however, important cost-sensitive, potentially high-volume, military and civilian applications of high-performance fibers (marine, submarine, land transport, and electronic) that do not require the ultimate mechanical strength and temperature resistance. Many applications can tolerate considerable

compromises in these characteristics, particularly if the resulting product permits exploitation of desirable chemical, electrical, magnetic, and thermal properties. Realization of these large-volume applications will require substantial reductions in the cost of fiber manufacturing for both government and commercial purposes.

Recommendation. A broader view should be taken of "high performance" to include properties of fibers other than mechanical ones. Effort should be directed toward large potential applications for high-performance fibers for which the highest attainable mechanical properties and temperature resistance are not essential and can be traded off for lower-cost products and/or products that exploit other useful physical and chemical properties. This effort justifies consideration of R&D directed toward achieving lower manufacturing costs for high-performance fibers for both government and commercial purposes.

Conclusion 3. Improvement of high performance synthetic fibers requires a combination of the materials science approach with the chemical and chemical engineering approaches.

Recommendation. Research on fibers should emphasize fundamental research directed at four specific interrelated technical issues for which this combined approach is essential.

- Fiber formation processes and mechanisms
- The effect of fiber processing on microstructure
- The relationship of microstructure to fiber properties
- Fiber-matrix interfacial interactions during fabrication and in service.

Conclusion 4. The universities' contribution toward the advancement of fiber science and technology is hampered by outdated equipment for teaching and research; the highly interdisciplinary nature of fiber R&D, which places extraordinary demands on the curriculum; and the lack of substantive high-performance fiber programs.

Recommendations. Increased industry and university interaction should be promoted in order to bring the facilities and personnel of both sectors to bear on the problems of equipment accessibility and interdisciplinary instruction. Specifically,

- A major equipment-oriented funding initiative should be undertaken, both by government and industry, to update fiber-related experimental facilities at U.S. universities.
- Curriculum changes and industrial participation in educational efforts should be implemented to deal with the interdisciplinary demands of the fiber industry.

Conclusion 5. Fiber-formation experiments that go beyond the feasibility stage—on into screening and end-use evaluation—involve the commitment of major capital resources, expertise, and man-hours. These resources are beyond the capabilities of most if not all universities and, in fact, beyond the capability of all but a few fiber producers and specialty consulting firms. This has obvious ramifications for the development of inorganic fibers of limited market appeal, which may be crucial to long-range national purposes; it has much less effect on the development of organic fibers, which have a broad commercial market.

Recommendation. The federal government must protect American security and economic interests by explicitly underwriting critical fiber development and production, rather than by the frequently used practices of short-term buys or incorporation into systems procurement contracts. Government support emphasis should be placed on the development of inorganic fibers because of their limited industrial base.

Conclusion 6. The advanced composites industry (and high-performance fibers manufacturing, in particular) is international in nature, with many U.S. fiber producers being foreign owned. As a result, substantial foreign capital has been invested in the United States, and there is potential for significant technology exchange on product and process development. This trend is expected to continue well into the twenty-first century.

Recommendation. The regulations concerning technology export need to be reviewed with this international aspect in mind, so that the United States can take full advantage of worldwide composites technology development as well as improve its strategic position.

Conclusion 7. Development of a new fiber in the quantities required for evaluation is expensive and time consuming. The same is true for qualification of a known fiber made by a new process.

Recommendations. Rapid and simple screening tests and characterization methods, which can be used on small quantities of fiber to predict the performance of large-scale product lots, should be developed. Standardization of fiber characterization and testing should be the subject of a major initiative involving government, industry, and universities.

In addition to the above general conclusions and recommendations, the following conclusions and recommendations apply to specific processing methods and/or specific fiber types.

Conclusion 8. Chemical vapor deposition (CVD) and single-crystal growth are well-demonstrated routes to the fabrication of continuous high-performance synthetic fibers. Pyrolytic conversion of precursor fibers (PCPF) and chemical conversion of precursor fibers (CCPF) are versatile methods of synthesis capable of producing fibers that are difficult or impossible to make by other methods. Their full potential remains to be developed.

**Recommendation.** Increased fundamental research on CVD and single-crystal processes should be encouraged for their potential to contribute to the development of high-performance fibers.

Increased attention should also be given to PCPF and CCPF as fiber-preparation processes. Their technological base should be strengthened by conducting a systematic study of various combinations of precursor fibers with a wide variety of reactants and processing parameters to make fibers of practical interest and to define the limits of these approaches.

**Conclusion 9.** Improved fibers are needed that are stable for long times at high temperatures.

**Recommendation.** Such improvements may result from R&D on fibers with major anisotropic crystalline components (such as alumina,  $\text{Al}_2\text{O}_3$ ; or mullite,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), if these components can be oriented with a major crystal axis aligned along the axial direction of the fiber. R&D with this in view should be encouraged.

**Conclusion 10.** Ceramic-matrix composites can provide significant performance advantages at relatively low temperatures, starting above the  $300^\circ\text{C}$  limit of polymer-matrix composites. The high performance and availability of carbon fibers could be exploited to achieve this goal. Although in the past higher-temperature goals were set for carbon fiber development, a more modest  $700^\circ\text{C}$  goal would be of practical significance and should be achievable.

**Recommendations.** R&D should be undertaken to develop advanced oxidation-resistant carbon fibers for use in ceramic-matrix composites at temperatures up to  $700^\circ\text{C}$ .

R&D should be carried out on fiber-interphase-matrix combinations to achieve environmental stability for applications at temperatures up to  $1200^\circ\text{C}$ . There is a high probability for success in achieving this goal by emphasizing coating and modifying existing fibers (silicon carbide, silicon nitride, mullite, and aluminum oxide).

**Conclusion 11.** Ceramic-matrix composites systems with temperature capabilities above  $1200^\circ\text{C}$  could provide great performance benefits to a wide range of significant aerospace programs.

**Recommendation.** Research on ceramic fibers should be undertaken to develop fibers with enhanced stability for use at temperatures above  $1200^\circ\text{C}$ . No single fiber system is expected to be useful for all composite matrices or environments. The objective should be to develop a selection of several high-performance ceramic fiber choices. Attractive oxide possibilities include yttrium aluminum garnet, spinels, and zirconates, as well as single-crystal mullite and alumina. Among the carbides, those of hafnium, zirconium, titanium, and tantalum have some promise, in addition to further potential improvements of silicon carbide. In addition to silicon nitride, various other nitrides appear interesting.

Conclusion 12. High-temperature metal- and intermetallic-matrix composites have great potential for military and aerospace applications; however, the availability of compatible fibers is severely hindering their development.

Recommendation. Fundamental studies on fiber-matrix compatibility in these systems should be expanded to include the study of fiber coatings and tailored interphase regions. The role of reaction products on the performance of both matrix and fiber also should be emphasized.

Conclusion 13. By attention to four specific aspects of carbon-carbon (C-C) composites, dramatic performance gains can be realized by using composites in advanced turbine engines and hypersonic vehicle applications.

- Since it is highly improbable that C-C composites can be made oxidation resistant for long-life applications, coatings will be needed to decrease the oxidation rate of carbon fibers at high temperatures by allowing a gradual degradation in the performance of the composite system instead of a catastrophic failure from a surface breach. Increased oxidation resistance of carbon fibers also would improve performance in existing single-cycle short-time applications where ablation and/or erosion occurs, as well as for low-earth-orbit spacecraft applications, where atomic oxygen resistance of C-C composites is required.

- The low density of C-C composites combined with the inherent good thermal conductivity of highly graphitic carbon makes possible a very high specific thermal conductivity material for one-dimensional heat transfer applications.

- With increasing progress in composite strength through matrix improvement, carbon fiber compressive strength will become the controlling factor limiting composite strength—an issue of particular importance for thin-walled C-C composite structures.

- The high processing temperatures used in fabricating C-C composites can affect the carbon fiber microstructure.

#### Recommendations.

- Develop increased oxidation-resistant carbon fibers by investigations that include doping, intercalating, or fiber coatings.

- R&D to develop high thermal conductivity carbon fibers should be continued. Improvement in the perfection of highly graphitic fiber structures is a promising approach.

- R&D to increase carbon fiber compressive strength for high-tensile-strength, high-modulus fibers should be undertaken. Cross-section shape modification of the fibers is a promising approach.

- Basic studies should be conducted to understand the microstructural changes that occur in carbon fibers during high-temperature C-C densification processing in order to avoid, or exploit, these processing effects on final composite properties.

Conclusion 14. Advanced polymeric matrix composite (PMC) materials are state-of-the-art structural materials that have many other potential applications in addition to aerospace. It is anticipated that substantial improvements will continue to be made in both manufacturing cost and mechanical performance. To the degree that these improvements result in significant improvements in their cost/performance ratio, the application volumes could rise exponentially (e.g., naval submarines and surface ships, automotive [commercial and combat vehicles], light bridges, lightweight weapon systems). Given the broad range of potential fiber performance, improvements in the fibers already commercialized (e.g., high modulus organics, glass, carbon fiber) and those currently under development (e.g., polybenzobisthiazole [PBZT], polybenzobisoxazole [PBO]), it is likely that many of the critical future application requirements can be addressed with these fibers.

Recommendation. A higher priority for future efforts on fibers for use in PMC's should be directed toward determining the performance limits of these commercial or developmental fibers rather than completely new fiber systems.

## HIGH-PERFORMANCE SYNTHETIC FIBERS FOR COMPOSITES

### INTRODUCTION

Fiber reinforcement of plastic, ceramic, and even metallic materials is a key technology for the automotive and aircraft industries and an enabling technology for numerous advanced systems, such as high-efficiency turbines and hypersonic aircraft. Although fiber-reinforced composite materials, such as fiberglass boats and automobile parts, and fiber-reinforced tires and drive belts, have long been articles of commerce, the development of so-called high-performance synthetic fibers has created a new generation of composite materials. This class of advanced composite materials exhibits physical properties that are vastly superior to those of the matrix material alone. These new composite materials are vital to the defense posture of the United States, but their future impact on the growth of our economy may be even more important.

Over the past 20 years a large number of high-performance fibers, comprised of materials as diverse as polyethylene and boron nitride, have been fabricated and characterized. A summary of the composition, relative properties, and availability of many of these fibers is given in Table 1.1. The motivation for this proliferation of potential fiber products is a combination of government-defined needs for aerospace and/or military programs and attractive commercial opportunities limited by the performance and availability of current materials. Of the many fibers described in the literature, only a few are truly commercial products; many are developmental and the vast majority are exploratory. Arbitrarily, "commercial" may be taken to mean a production capacity of at least 10,000 pounds per year, "developmental" a capacity for about 1000 pounds per year, and "exploratory" may mean that only a few grams of the fiber have ever existed.

High-performance fibers possess reinforcing properties (tensile strength, stiffness, thermal stability, etc.) that significantly exceed those of the traditional fibers that have been used for many years (textile-grade



nylon or glass fibers). Currently, the principal applications of high-performance, fiber-reinforced composite materials are structural, particularly in aircraft and spacecraft where their light weight, combined with superior stiffness and strength, makes them preferable to metal. Thus, both performance and fuel economy can benefit from increased utilization of these materials. Since high-performance fibers are extensively used in aircraft structures, it is imperative to have a sound foundation in fiber technology and domestic production of these high performance fibers if the United States is to remain a world leader in aircraft production.

TABLE 1.1 High-Performance Fibers

| <u>Fiber Chemistry</u>         | <u>Formation Process</u> | <u>State of Availability</u> | <u>RT Tensile</u> |                  | <u>Use T</u>               | <u>1990</u> |
|--------------------------------|--------------------------|------------------------------|-------------------|------------------|----------------------------|-------------|
|                                |                          |                              | <u>Modulus</u>    | <u>Strength</u>  | <u>O<sub>2</sub> Inert</u> | <u>Cost</u> |
| Aramid                         | Solvent Spin             | +                            | -                 | 0                | - -                        | -           |
| LCpolyester                    | Melt Spin                | +                            | -                 | 0                | - -                        | -           |
| Polyethylene                   | Gel Spun                 | 0                            | -                 | 0                | - -                        | 0           |
| PBO, PBZT                      | Solvent Spin             | -                            | 0++               | 0                | - -                        | 0++         |
| C Fiber, PAN                   | Polymer Pyrolysis        | +                            | 0                 | 0++              | - +                        | 0++         |
| C Fiber, Pitch                 | Meltspin Pyrolysis       | 0                            | +                 | 0                | - +                        | +           |
| Mullite                        | Pyrolysis                | +                            | 0                 | 0                | 0 0                        | 0           |
| Alumina                        | Pyrolysis                | +                            | 0                 | 0                | 0 0                        | 0           |
| Si <sub>3</sub> N <sub>4</sub> | Polymer Pyrolysis        | -                            | 0                 | 0                | +                          | +           |
| SiC                            | Polymer Pyrolysis        | 0                            | 0                 | 0                | +                          | +           |
| SiC                            | CVD                      | 0                            | +                 | 0                | +                          | +           |
| B                              | CVD                      | 0                            | +                 | 0                | +                          | +           |
| BN                             | Chemical Conversion      | -                            | -                 | -                | +                          | +           |
| B <sub>4</sub> C               | Chemical Conversion      | -                            | 0                 | -                | 0 0                        | ++          |
| ZrO <sub>2</sub>               | Pyrolysis                | -                            |                   |                  |                            | +           |
| Alumina/Zirconia               | Pyrolysis                | -                            |                   |                  | +                          | +           |
| TiB <sub>2</sub>               | CVD                      | -                            |                   |                  | +                          | +           |
| Glass                          | Melt Spun                | +                            | -                 | 0                | - -                        | - -         |
| <br><b>KEY:</b>                |                          |                              |                   |                  |                            |             |
|                                |                          | +                            | 0                 | -                |                            |             |
| Availability lb                |                          | ≥10 <sup>5</sup>             | > <               | ≤10 <sup>3</sup> |                            |             |
| Modulus Mpsi                   |                          | ≥50                          | > <               | ≤20              |                            |             |
| Strength Kpsi                  |                          | ≥750                         | > <               | ≤250             |                            |             |
| Use T °C                       |                          | ≥1000                        | > <               | ≤300             |                            |             |
| Cost \$lb                      |                          | ≥100                         | > <               | ≤15              |                            |             |

# PRESENT MATERIALS: AN OVERVIEW

Most materials used in structural applications are either polymers, metals, or ceramics, and in many present applications these materials perform satisfactorily in their unmodified or unreinforced form. When the thermal stability and strength of the material are not critical, low-cost polymeric materials such as acrylates, epoxies, and polycarbonates can perform acceptably. Likewise, metals such as aluminum, steel, copper, or tungsten are adequate for lightweight structural components, tooling, electrical conductors, and lamp filaments, respectively. Because cost is the controlling factor, the present performance of many ceramic structural products such as window glass, structural bricks, and cement blocks is considered satisfactory. However, in many applications where performance is the controlling factor (i.e., aerospace, transportation, underwater vessels), advanced structural materials are needed that are stronger, stiffer, lighter weight, and more resistant to hostile environments. Unreinforced, the polymer, metal, and ceramic materials available today cannot meet many of these requirements. This is especially true if the structural component must be exposed to extremely high temperatures for extended periods of time. The graph shown in Figure 1.1 provides the approximate temperature limits for the use of various structural materials.

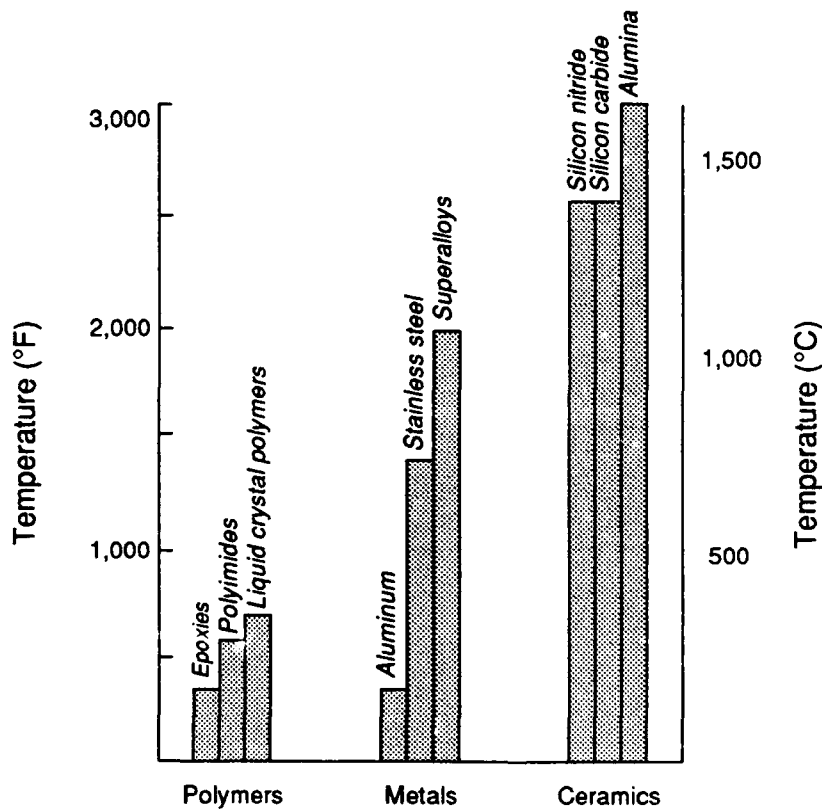






FIGURE 1.1 Maximum-use temperatures of various structural materials.<sup>1</sup>

### CHARACTERISTICS OF MATERIALS IN FIBER FORM

Natural fibers such as cotton and wool are some of the oldest materials. These fibers were used by early man when strength and light weight were critical. However, only in the past 50 years, with the development of analytical techniques such as X-ray diffraction, has the reason for the unusual properties of materials in fiber form been understood. Scientists now know that the molecules within fibers tend to align along the fiber axis. This preferred alignment makes the strength and modulus (stiffness) of both natural fibers and synthetic fibers superior to the same material in a randomly oriented bulk form. As an example, Table 1.2 shows the strength and modulus of a typical polymer in various forms. While the strength of an injection-molded polyamide plate is only 0.08 GPa, the tensile strength of the same polymer is over five times greater when it is extruded into a textile-grade fiber. If this same textile-grade fiber is stretched in an extensive drawing process, an industrial-grade tire cord fiber can be produced that is 10 times stronger and nearly twice as stiff as the injection-molded polymer. Chemically, all of these materials are identical, differing only in the orientation and structure of the solid polymer. When both natural and synthetic polymers are extruded and/or drawn into fiber form, the processes of extrusion and extension orient the structure along the fiber axis. This results in high strength and increased stiffness for much the same reason that an oriented mass of strings (a rope) is stronger and stiffer than the same mass of strings with no orientation.

TABLE 1.2. Properties of Polyamid in Various Forms

| Form                   | Tensile Strength (GPa) | Tensile Modulus (GPa) | Orientation  |
|------------------------|------------------------|-----------------------|--|
| Injection molded       | 0.08                   | 2.5                   |  Random       |
| Textile-grade fiber    | 0.43                   | 2.5                   |  Medium       |
| Industrial-grade fiber | 0.92                   | 4.5                   |  High         |
| Kevlar®†               | 3.50                   | 186.0                 |  Near perfect |

†Trademark of E.I. DuPont de Nemours and Co.

Rigid, liquid-crystal-forming polymers (e.g., aramid fibers) can develop nearly perfect orientation and alignment during fiber formation. This allows

a kilogram of fibers formed from this rigid polyaramide molecule to be five times stronger than a kilogram of steel and still be five times as stiff. Since the density of aramide fiber is only one-fifth that of steel, this new class of synthetic high-performance fibers already is an obvious replacement for metal in many applications.

Brittle materials, like carbon, also have a higher strength and stiffness when formed into fibers. High-performance carbon fibers formed from pitch are now available commercially with a tensile strength of 3.9 GPa. This is approximately 1000 times greater than the strength of unoriented carbon in bulk form. In the case of brittle materials, the higher strength of fibers is caused by two factors. First, like polymeric fibers, the molecular structure and orientation are improved by the fiber-formation process. Second, since the failure of brittle objects is dominated by flaws, the small size of fibers limits the size of the flaws that can exist. Thus, in addition to forming a more perfect structure, brittle materials in fiber form contain smaller flaws, further enhancing the tensile strength.<sup>2</sup>

Unfortunately, the increased tensile strength of fibers does not come without a penalty. Fibers, like rope, display this increased strength only when the load is applied parallel to the fiber axis. Even though the tensile strength parallel to the fiber axis increases as the orientation and structure become more perfect in the fiber direction, this same increase causes a decrease in strength perpendicular to the fiber axis. For example, the strength of a carbon fiber perpendicular to the fiber axis is 10 times less than the strength parallel to the axis. Also, as the orientation of a fiber increases, it often becomes brittle, making it more susceptible to damage by abrasion. Thus, to take advantage of the high strength of fibrous materials in a structure, the fibers must be oriented in the direction of the applied load and separated to prevent damage by abrasion.

Mechanical reinforcement of matrices can also be accomplished by short, randomly oriented fibers, by crystal "whiskers," or by particulates. These types of reinforcement offer directionally independent (isotropic) reinforcement, but the degree of reinforcement is not as great as that obtainable from longer continuous filamentary fibers. This report is concerned principally with high-performance continuous fibers.

### **ADVANCES IN FIBER TECHNOLOGY**

Advances in the performance of fibers have come about because of continuity of effort on fiber materials and fiber-processing research and development. This is illustrated by Figure 1.2 for the case of organic polymer fibers; and similar illustrations apply to other types of fibers. In the early 1920s the first synthetic fibers were produced from cellulose. Because this natural polymer degrades before it ever melts, this early synthetic fiber was precipitated from a concentrated polymer solution. After precipitation the cellulose fibers had to be drawn in order to orient the polymer molecules and improve the mechanical properties. Nylon, one of the

earliest synthetically produced polymers, was introduced as a fiber in the 1940s. Since this polymer would melt before it degraded, a melt spinning process was developed. This new fiber-formation process allowed some limited orientation to be introduced during extrusion, further increasing the fiber strength. With the recent discovery of liquid crystal polymers, fully oriented fibers can now be spun. Thus, as Figure 1.2 indicates, the mechanical properties of fibers have improved dramatically over the past 50 years, and the major breakthroughs have been due to the development of new materials and processing techniques. However, as with other technologies, these breakthroughs were the direct result of continuing research and development. Without continuity in effort, breakthroughs in any technology are unlikely.

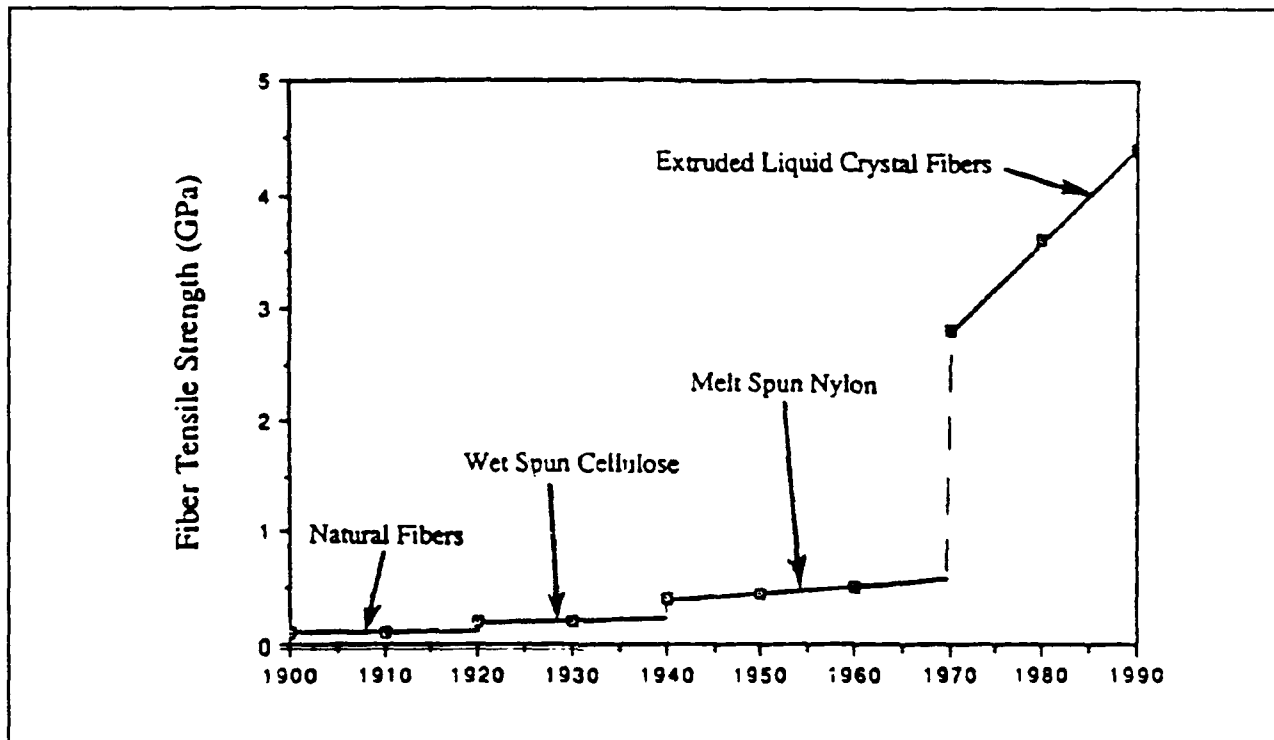


FIGURE 1.2. Strength of typical commercial organic fibers.

During the period shown in Figure 1.2, the size of the U.S. synthetic fibers industry also grew dramatically. In 1988 the industry produced over 9 billion pounds of synthetic fibers for industrial and textile end uses,<sup>3</sup> accounting for about 24 percent of the total world production. Because of this high production volume, the U.S. synthetic fibers industry is one of the most efficient in the world, in terms of pounds produced per worker, and is a vital part of the domestic economy. Even though the total world usage of high-performance fibers was only about 11 million pounds in 1988, it has consistently grown at a rate of 10 to 20 percent per year.

High-performance fibers represent a major area of growth for the synthetic fibers industry, and a number of these fibers are already available commercially. The potential market for a low-cost, high-performance fiber is enormous. In fact, a large market already exists for a low-cost reinforcement fiber. During 1988, 3.6 billion pounds of glass fiber, a textile-grade nonsynthetic fiber used in low-strength structural composites, was produced worldwide, an indication of the potential market that could be available, at least in part, to a low-cost, high performance fiber.

Projections of world demand for advanced composites indicate that it will reach approximately 500 million metric tons by the early decades of the twenty-first century, of which industrial and other applications will grow to 55 percent of market share while the aircraft/aerospace market share will drop to 45 percent. At a 60 percent loading factor, this amounts to a demand for approximately 300 million metric tons of high-performance fibers in the above-mentioned time period. It is important to note that this is a conservative estimate based on the current price of advanced fibers—\$15 to \$20 per pound. It is forecast that if the cost of these fibers could be reduced to a few dollars per pound, the demand would be a factor of 10 higher.

To increase productivity and reduce manufacturing and processing costs, synthetic fibers are normally produced and sold in multifilament bundles. As Figure 1.3 shows, there is often a trade-off between the size of this bundle of fibers, final fiber properties, and fiber cost, even for current high-performance fibers.

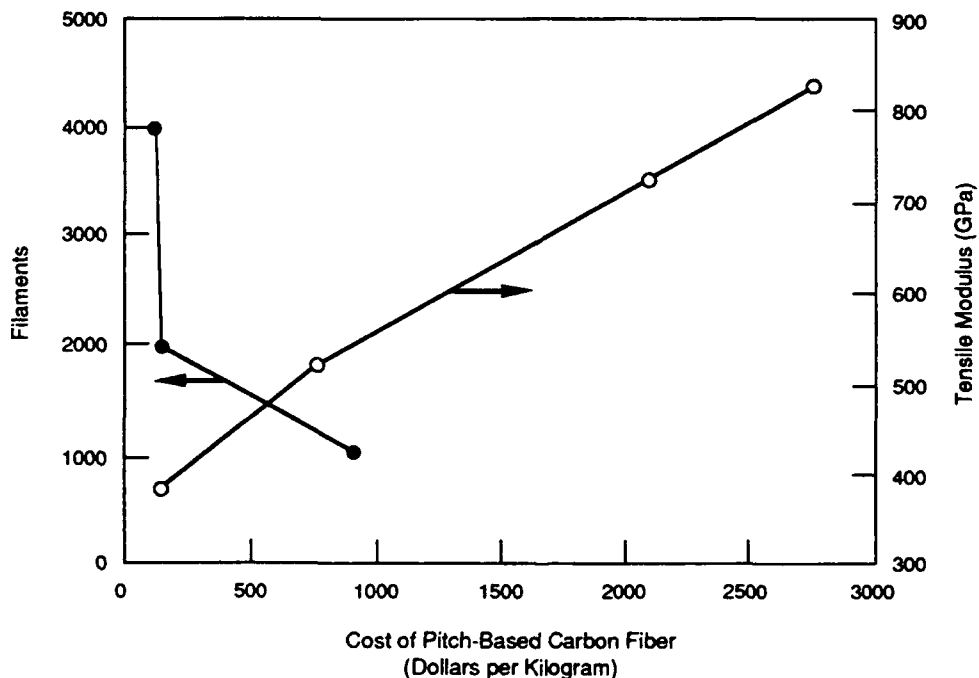


FIGURE 1.3 Fiber price versus bundle size and fiber physical properties.

### TYPES OF HIGH PERFORMANCE FIBERS

Today, numerous types of high-performance fibers are commercially available. These fibers range from polymeric fibers, such as aramid and extended-chain polyethylene, to carbon fiber, boron fiber, and ceramic fibers such as silicon carbide, and alumina. As Figure 1.4 shows, when a load is applied parallel to the fiber axis, all of these fibers are much stronger and more rigid (per given mass of a material) than traditional metals such as steel or aluminum. However, each of these high-performance fibers has certain additional advantages. For example, in oxygen-free environments, carbon fibers can retain their strength at extremely high temperatures. Polymeric fibers are much lighter than carbon and ceramic fibers and transparent to radar. Ceramic fibers, on the other hand, are resistant to oxidation but lose strength at high temperatures. The advantages and deficiencies of these and other high-performance fibers are detailed in later sections of this report.

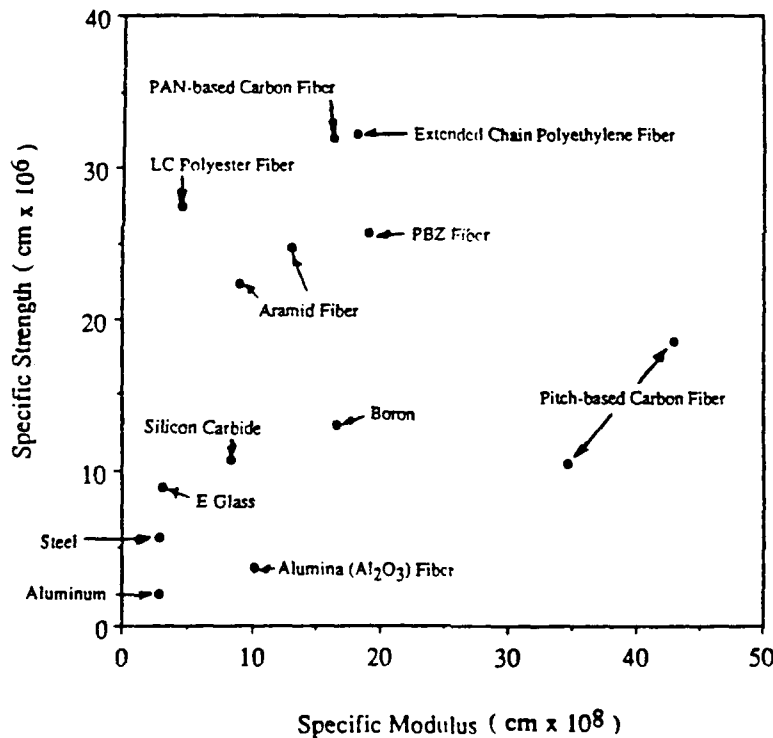


FIGURE 1.4. Specific strength and modulus of high-performance fibers and other materials "specific property" means the property divided by the density.

### FIBER-REINFORCED COMPOSITES

In a composite material the fibers are surrounded by a thin layer of matrix material that holds the fibers permanently in the desired orientation

and distributes an applied load among all the fibers. The matrix also plays a strong role in determining the environmental stability of the composite article as well as mechanical factors such as toughness and shear strength. Since the reinforcing fibers can be oriented during fabrication of an item, composites can be tailored to meet increased load demands in specific directions. The combined fiber-matrix system is an engineered material designed to maximize mechanical and environmental performance.

There is an important, but not generally well understood, difference between the development time for traditional materials compared to that for high-performance fibers. Because a composite material is a complex system of two components coupled at an interface, the time required to develop and optimize new high-performance fibers for a particular application is much longer than that needed for the development of traditional materials. For composite applications it normally takes from 5 to 10 years to develop a new high-performance reinforcing fiber. This development time differs very markedly from the 1- to 3-year development period common to many government projects.

Composite materials containing fibers (whether they be short staple fibers, whiskers, or fibers in continuous filament form such as roving or textiles) provide considerable flexibility in the design of structures. Because of this, composites of inexpensive glass fibers embedded in a plastic-matrix material have been used extensively in medium-to-high-volume applications by the transportation, construction, and recreation industries for over 40 years in applications such as auto body panels, boat hulls, and chemical tanks. However, high performance fibers dramatically expand the opportunities for composite materials. When high-performance fibers, such as carbon or polyaramide, at fiber loadings typically greater than 45 percent, are surrounded by the same plastic matrix, the material becomes an "advanced composite." Thus, in many ways, advanced composite materials represent a major breakthrough for a composite material technology that has been extensively utilized for many years. It is the added strength and stiffness of these new reinforcing fibers that allows the new advanced composites to outperform current metal and metal alloy structures.

By dispersing fibers or particles of one material in a matrix of another material, today's designer can obtain structural properties that neither material exhibits on its own.<sup>4</sup> For example, a metal alloy selected for its resistance to high temperature but having low resistance to creep at use temperature can be reinforced with fibrous inorganic oxide fibers to provide enhanced creep resistance and still be stable at high temperatures. A ceramic matrix, brittle and sensitive to impact or fracture induced by thermal stresses, may be reinforced with ceramic fibers to increase its resistance to crack propagation, providing greater toughness and protecting against catastrophic failure. The addition of reinforcing fibers to provide equal mechanical properties at a greatly reduced weight is often an important reason for choosing composites over traditional structural materials. Another vital consideration is the substitution of readily available materials for critical elements in short supply or those available only from foreign sources. Composite materials made from abundant, domestically available materials such as carbon, polymers, ceramics, or common metals can often outperform these



imported strategic materials. In defense applications this substitution could be vital since even the nickel, chromium, and cobalt needed for common steel alloys are now imported.<sup>5</sup> Even advanced ceramic composites, toughened and less likely to fail catastrophically, may provide a viable alternative to some of these imported materials.<sup>6</sup> Reinforced polymers have been making inroads in the metal alloy market for years. In fiber-reinforced polymers, even fatigue resistance is improved significantly. According to B. R. Norton,<sup>7</sup> the improved strength and stiffness properties of fiber-reinforced polymers allow rotational components fabricated from these materials to operate much faster than those of steel alloys. Finally, unlike conventional materials, it is relatively simple to incorporate sensors and optical fibers into fiber-reinforced composites to monitor applied loads and detect damage, creating "smart" structures.

In summary, some of the specific advantages of fiber-reinforced composites are as follows:

- Higher specific modulus and strength values
- Lighter weight
- Controllable ("tailorable") properties
  - Toughness
  - Electrical and thermal conductivities
  - Thermal expansion
  - Stiffness
- Resistance to corrosion
- Better resistance to creep at high temperatures
- Substitution for critical or strategic materials
- Creation of multipurpose or "smart" structures

The recently published Handbook on Composites<sup>8</sup> is an important reference for current information on composites and basic materials used in composites, including fibers and fiber properties useful in the design or development of composites. Also, an especially pertinent broad review of present materials and needs for the future was published in the October, 1986, issue of Scientific American.<sup>9</sup>

### **Projections for High Performance Fibers**

The fiber research needed will depend on both the application and the fiber in question. For example, even though carbon fibers are commercially available, research directed toward product improvement and cost reduction will still yield significant payback. Research already being funded by the federal government is yielding progress in ceramic fibers and whisker technology, but new applications, such as the hypersonic transport vehicle, may require significant advances in this art. Present metals and superalloys cannot withstand the operating temperatures predicted for the National Aerospace Plane (NASP), and the use of fiber-reinforced composites is the likely solution. As existing composite materials are exposed to ever-increasing temperatures, it appears that present fiber reinforcement materials will not meet many of these requirements and that new fibers and whiskers are probably needed. At elevated temperatures, present high-performance fibers

exhibit excessive grain growth or oxidize, resulting in deficiencies such as low modulus or strength properties, excessive creep rates, thermal expansion mismatch, or reaction with matrices. Other potential applications for high-performance fibers include applications such as electronic or weapons systems, where the ability to match the thermal expansion coefficients of adjacent components and to dissipate heat is critical. This may be the major future market for pitch-based carbon fibers, which can develop a thermal conductivity that is at least three times greater than copper. The application of these fibers to dissipate heat could revolutionize both the size and operating speed of computer and electronic systems.

In all these projected areas for high-performance fiber development, it is critical that support be continuous and that the longer time required to develop these fibers for composite applications be recognized. Unfortunately, development of new fibers with promising properties is costly. Thus, federal funding may be necessary both to ensure a domestic source for these fibers and to support the research and development needed to improve manufacturability and reduce costs. When this is the case, it is especially important for the government sponsor and the funded development group to establish a relationship based on cooperation, rather than on strict oversight, to accelerate fiber development and minimize management costs.

Present performance-driven applications provide the opportunity and the need to develop a strong domestic technology base in the high-performance fibers required for composite materials. Future high-volume markets such as automotive and construction applications will be cost-driven, and it is vital that the domestic fiber industry be prepared to aggressively compete in these markets. It is this potential for tremendous future growth, coupled with the fact that high-performance fibers are critical for many present high-technology products, that makes basic fiber research and the health of our domestic fiber industry vital to both the U.S. economy and our national security.

Because the composites industry is highly international, extensive fiber science/technology bases also exist in Western Europe and Japan, where there are strong commitments to support the development of high-performance fibers. Unless steps are taken to strengthen our domestic fiber science/technology base, to facilitate its industrial application, and to broaden the industrial base for high-performance fibers, the United States might lose its present competitive position in this key industry.

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## **High-Performance Fiber Materials: Applications, Needs and Opportunities**

### **INTRODUCTION**

Fiber-reinforced composites have been an important industrial product for many decades. Structural applications of these composites have dominated the development of fibers throughout this period. This fact is recognized in the following presentation of the state of the art of fiber where—unless otherwise stated—"applications" refer to structures or components demanding high-performance mechanical properties. High performance fibers used in these applications are often classified by the matrix used to support them. This is a convenient classification because it effectively specifies the temperature rating of the composite structure: polymeric—ambient to 800°F, metal matrix—1500° to 2500°F, and ceramic—2000° to 3000°F. The various fiber types will therefore be discussed based on this classification.

It should be noted that there are many current and potential applications of fiber-reinforced composites that cannot be called "structural" because their function is mainly to exploit some other physical property rather than only mechanical strength. To emphasize the importance of this class of fibers, a separate section is devoted to a discussion of fibers used for these applications.

### **HIGH-PERFORMANCE FIBERS FOR POLYMERIC-MATRIX COMPOSITES**

In the United States, reinforced plastics represent a very large market of approximately 2.3 billion pounds/year, valued at about \$2.5 billion. A very important high value-added, but relatively low-volume, sector of the reinforced plastics market is the advanced composites market. Advanced composites are defined as products that utilize substantial percentages (50 to 70 percent by weight) of high-performance fiber reinforcements, having

excellent mechanical properties, in combination with organic, metal, or ceramic matrices. Organic-matrix composites or polymeric-matrix composites (PMCs) constitute by far the largest component of the advanced composites market.<sup>(1)</sup>

PMCs, which are broadly used throughout the world in applications where strategic weight and performance characteristics are important, are projected to experience steady growth over the next two decades. While the aerospace business has been the key industry fueling this growth, automotive, industrial, and leisure products represent important market segments. The relative importance and growth of each of these markets depend on critical technical advances in two important areas: (1) improving the ultimate performance of material systems while reducing cost, and (2) improving fabrication technology for making parts in a cost-effective way. In 1988 the estimated worldwide consumption of advanced PMCs was 25 million pounds (12 million to 18 million pounds of high-performance fibers), representing a \$1.5 billion business that is growing 16 percent annually.

PMCs are attractive because they offer a combination of the advantages shown in Table 2.1, produced by integration of constituent fibers and resins with materials design and fabrication at acceptable cost.

TABLE 2.1. Advantages of PMCs

|  |  |
|--|--|
| Good specific stiffness and strength         | Fatigue resistance                                   |
| Low density                                  | Low coefficient of thermal expansion                 |
| Ease of fabrication                          | Creep and creep fracture resistance                  |
| Relatively low raw materials cost            | Excellent in-service experience                      |
| Potential for lower cost fabrication methods | Property "tailorability" to application requirements |
| Corrosion resistance                         |  |

### Major Current Fibers

#### Properties; Demand

PMCs are made by combining reinforcing fibers containing high strength and stiffness properties with polymeric matrices to produce tailored materials with combined performance not possible with either constituent alone. The dominant fibers used (more than 99 percent) in PMCs are glass, carbon, and aramid fibers. Other fibers that have more limited usage are boron, silicon carbide, alumina, and, more recently, liquid crystalline fibers—that is aromatic polyesters, poly(paraphenylene), benzobisoxazole (PBO), and extended-chain polyethylene.

The matrix resins used in PMCs are of two types: thermosets and thermoplastics. The most common thermosets are polyester, vinyl ester, epoxy, bismaleimide (BMI), and polyimide (PI). The major classes of thermoplastics under evaluation today include polyether ether ketone, polyamide,

polyamideimide, polyimide, polysulfone, and polyphenylene sulfide. Epoxy resins represent the dominant matrix in use today, and they have established a very large data base and track record in the field.

Carbon fiber represents the dominant fiber in the advanced composites industry. It has been used in the industrial, recreation, and aerospace markets. Figure 2.1 shows U.S. carbon fiber consumption by major market segment from 1976 through 1988.

### *Applications*

Glass/epoxy composites are used in printed wiring boards. They are also used in the automotive industry in limited semistructural and structural applications such as body panels and composite springs. Glass/vinyl esters and/or polyester are used in the chemical industry for corrosion-resistant applications. Carbon fiber, aramid, and some of the other high-performance fibers (boron, silicon carbide) are used in recreation, industrial, and aerospace products, but they are most effective for uses in which performance is the primary consideration and cost the secondary.

The recreation market represented the first large-volume usage of carbon fiber. Typical applications include tennis rackets, fishing rods, golf shafts, and sailing masts. This market is nearly at a saturation point, and it is expected to grow at a very slow rate in the future. In recent years much of the manufacturing of composite recreation articles has shifted to the Far East, thereby contributing to the recreation market's rapid growth and its decline in the United States to the smallest of the three major market segments.

During the past few years, the U.S. industrial market segment has experienced gradually increasing growth rates, and it is now the second largest of the three major market segments. The industrial market uses chopped carbon fibers primarily for electromagnetic interference/radio frequency (EMI/RFI) shielding applications. Previously, it was anticipated that large-volume applications would emerge for automotive applications, but the combination of high material cost and lack of high-speed fabrication technology has prevented this from happening. Continued rapid technology growth should minimize these factors in the future. Some limited automotive applications have been commercialized, such as overwrapped carbon/epoxy aluminum driveshafts.

The aerospace/aircraft market is currently the largest U.S. sector for carbon fiber composites. This market sector has driven the overall industry from the standpoints of performance, quality, and capacity and will continue to do so well into the next century. For example, the major advances in carbon fiber properties and new product development, the installation of new carbon fiber capacity, and the drive to install domestic precursor capacity can all be directly tied to rapid penetration of carbon fiber into the aerospace/aircraft market. Carbon fiber composites are now being used in the

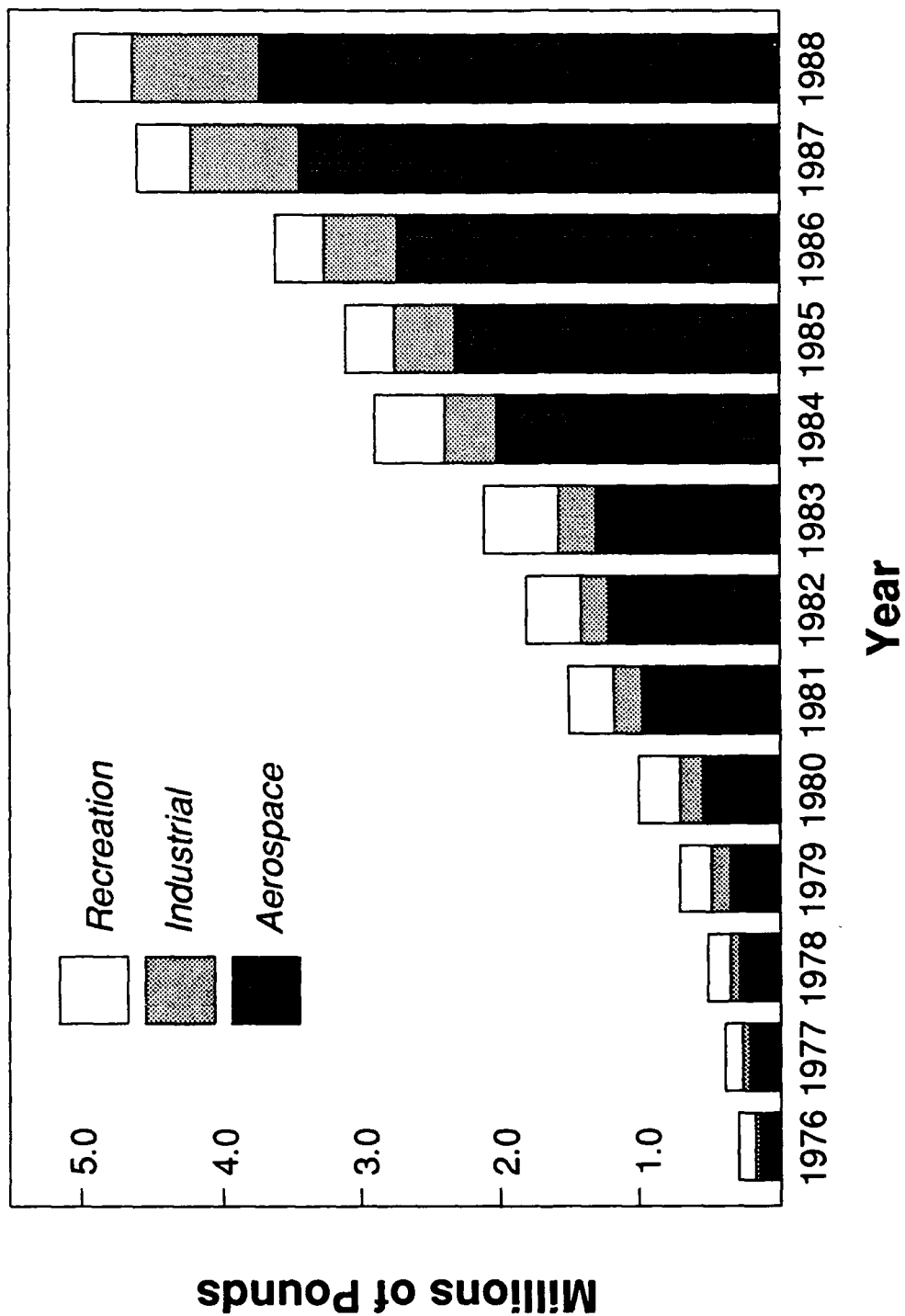


FIGURE 2.1 U.S. Carbon Fiber Consumption by Major Market Segment

following major aerospace areas: aircraft and helicopters, missiles and spacecraft, and brakes and tooling for parts fabrication. Figure 2.2 illustrates the rapid growth in aerospace carbon fiber consumption during the period since 1976 projected through 1990.

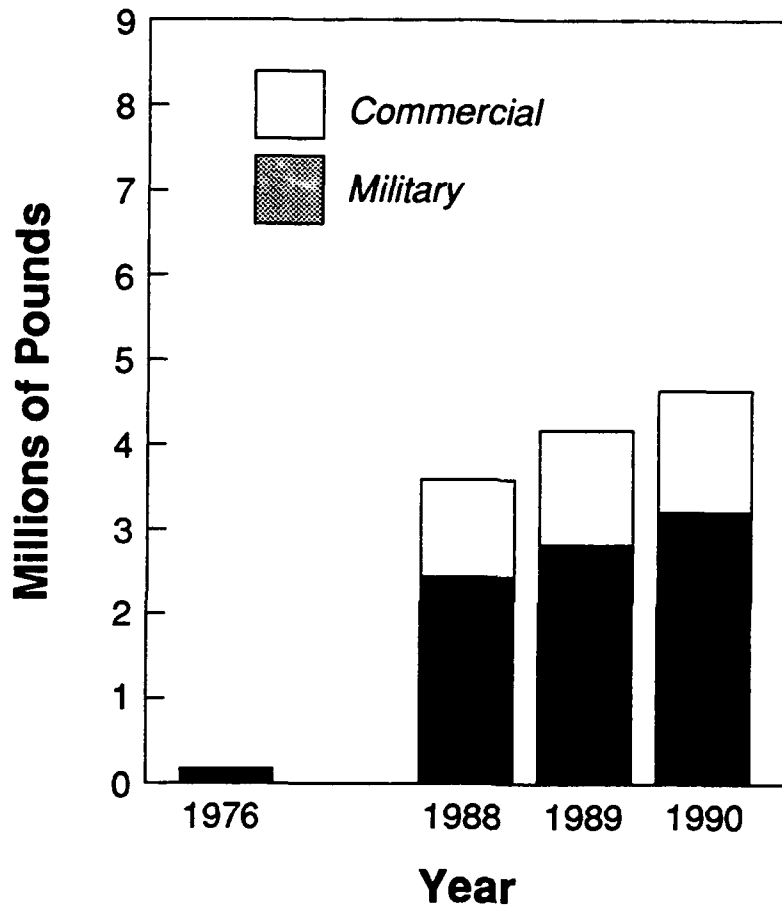


FIGURE 2.2 U.S. Carbon Fiber Consumption Aerospace Market

*Industrial Sources; Industry Structure; Market Situation*

The advanced composites industry (particularly, the PMCs component of that industry) is extremely international in nature. For quite some time, major U.S. manufacturers (polymers, fibers, intermediate products) have had close business arrangements with Japanese and European manufacturers, which have included technology transfers as well as joint ventures. This trend is expected to continue partially in support of the continuing internationalization of the aircraft/aerospace industry. While different geographical territories have historically had different market strategies (i.e., Japan historically has a heavy interest in recreation products in contrast to emphasis on aerospace products in Western Europe and the United States), all international companies seem to be addressing the same critical technical and economic issues.



However, with respect to applications development, Western Europe has taken a more aggressive posture toward aircraft structure and Japan has been more proactive in the area of nonaerospace industrial parts. Examples of the latter include robotics and mechanical tools. Since the market situation for carbon fibers is more highly developed and much more competitive (at least in the United States) than any other class of high-performance fibers, a detailed discussion seems warranted.

Polyacrylonitrile (PAN)-based carbon fiber represents approximately 90 percent of all carbon fiber sales worldwide, with the remainder consisting primarily of pitch-based fibers. During the past several years, PAN-based carbon fiber capacity has grown rapidly as companies expanded their capacity to establish market position and meet the growing demand for carbon fibers. For example, in 1980 the total free world capacity<sup>2</sup> was just over 1400 metric tons (3 million pounds). Today, the free world capacity is approximately 12,100 metric tons (27 million pounds); U.S. capacity is estimated at around 5000 metric tons (11 million pounds). Meanwhile, the free world carbon fiber demand grew at an annual rate of over 20 percent, from an estimated 900 metric tons (1.2 million pounds) in 1980 to about 4500 metric tons (10 million pounds) in 1988.<sup>3</sup> Because the increments of new carbon fiber capacity were large relative to the total carbon fiber demand during this time period, there have been periodic capacity excesses and periodic fiber shortages. Indications are that during the next 5 to 10 years carbon fiber demand will grow at a slightly slower rate, ranging somewhere between 10 to 15 percent annually. Since most major U.S. carbon fiber producers have announced substantial capacity expansions that will be brought on stream in the early 1990s, the growth in fiber capacity is expected to continue to exceed the growth in fiber demand.

Early PAN-based carbon fiber capacity was concentrated in the United Kingdom and Japan, but today over one-third of the capacity is in the United States. The U.S. share of world capacity should continue to increase, in large part due to the growing volumes of carbon fiber required to meet expanding Department of Defense (DOD) requirements. Until recently, almost all PAN precursor was produced outside the United States, either in Japan or the United Kingdom. However, with the passage of the DOD PAN domestic precursor directive,<sup>4</sup> all major U.S. carbon fiber suppliers have built, are building, or have announced an intention to build their own PAN production units. This will be a major disruption for the industry (capital installation, product requalification, etc.) through the end of the century.

Pitch-based carbon fibers are not as well established as PAN-based fibers, and currently there is only one commercial supplier of high-performance continuous fibers in the United States (Amoco Performance Products, Inc.). However, technical activity in this area was intense in the past decade, particularly in Japan, and there are now several Japanese suppliers that are beginning to supply material to the U.S. market. Pitch-based carbon fibers are now being viewed as a viable material in high-modulus, high-conductivity application areas where low-to-medium strength is acceptable.

Recently, the carbon fiber and PMC industries have undergone significant realignments, as evidenced by BASF's purchase of Celanese's composite business, Amoco's purchase of Union Carbide's composites operations, BP's takeover of Hitco's advanced composites business, Akzo's purchase of Great Lakes and Wilson Fiberfil, and ICI's purchase of Fiberite and LNP from Beatrice. These realignments are resulting in a composites industry comprised of stronger competitors that are clearly forward looking in their strategic objectives and investing for the future.

#### *Future Application Challenges*

The range of future applications for PMCs has the potential to be very large and to encompass a multitude of end-use sectors; some of these end uses, such as military applications will be driven primarily by performance, and the others, such as automotive and general industrial, will be driven primarily by cost.

In order for the PMC sector to increase its market share in its current applications and to grow into new applications, it needs to overcome some key hurdles—product performance, fabrication, and economic issues. Fiber developments can play an important role in all of these issues.

It is clear that PMCs will continue to increase their usage as a structural reinforcing material on military aircraft as long as the criteria of reduced weight and higher performance remain key goals. For example, the Air Force is currently funding a number of research initiatives as part of its Ultralightweight Structures Program in which the goal is to assess the feasibility of a 50 percent decrease in the structural weight of baseline vertical takeoff and landing fighter and transport aircraft. The rate of penetration against competitive materials will be determined by how quickly some of the technical hurdles such as increased damage tolerance, overall balance of properties (i.e., improved compression performance), and high temperature performance are resolved. Utility in space applications, where a critical application is the space station, will also increase as PMCs with increased stiffness and reduced coefficient of thermal expansion are commercialized.

Two areas of the military in which PMCs have not been used extensively but are projected to be in the future are land- and sea-based vehicles. The need for next-generation equipment (e.g., greater weapons payloads, faster speed, signature reduction) as well as the advantages and disadvantages of PMCs against metals in these end uses are similar to those found in aerospace vehicles and aircraft. For example, critical problems of PMCs that are under study by the Navy for surface and submarine applications include the following: fabrication of very thick sections (4 to 13 inches), very high compressive loadings, fire resistance, very high static and shock loads, and long-term performance (greater than 20 years). The need to resolve these problems, coupled with the small number of new ships and submarines being built, means that PMCs will see only a small usage for these purposes over the next decade. The long-term consumption, however, could be very large and could easily be equal to that projected for aerospace and aircraft applications.

The broad range of reinforcing fibers that are capable of being used in PMCs offers the potential for substantial PMC consumption in large, nonaerospace, nonrecreation markets where PMCs previously have had either limited or no significant utilization. These markets include general industrial (in addition to the current EMI/RFI applications), automotive, and civil engineering. Within these markets, there is a whole host of applications for which PMCs, based on today's technology, meet the critical technical requirements of the application. Examples of the broad range of applications would include robotics, ropes and cables, heat exchangers, bridge decking, and reinforced concrete. The key to increased consumption in these diverse end uses is reduced raw material costs and improved fabrication technology; with current raw material costs (fibers are a key component of the cost) and relatively long fabrication cycles, the PMC use is limited at best. However, with the commercialization of a very low cost PAN- or pitch-based carbon fiber (in the \$5 to \$8 per pound range), for example, some of these applications would become economically viable. Another approach to reducing fiber costs is the hybridization (or mixing) of two fibers in a composite structure in order to meet the technical requirements of the part while minimizing cost. The hybridization of glass and carbon has been used in the automotive industry to take advantage of the high strength and low cost of glass with the very high modulus of carbon.

In addition to product and fabrication issues, a number of economic issues must be addressed because PMCs are generally more expensive to purchase and/or fabricate into final parts than metals. Even though relatively low raw material costs are considered an advantage for PMCs (see Table 2.1), these materials are still too expensive to permit extensive development of new applications in the industrial, automotive or civil engineering industries where performance is not the principal concern. As pointed out in Chapter 1, lower cost routes for producing reinforcing fibers must be developed if these new applications are to be achieved. Because of the drive to produce high-performance products for the aerospace/aircraft industry, PAN- and pitch-based carbon fiber suppliers have not undertaken a major initiative in this direction.

Besides reductions in fiber costs, improved parts fabrication technology that approaches the rates currently achievable with metals must be developed. Stampable thermoplastics offer a real potential to significantly improve this latter area. Advanced design techniques combined with novel fabrication methods have the potential to reduce counts scrap and parts through structural integration to improve cost competitiveness. Advances in economics should make it possible for PMCs to penetrate for the first time into applications in the industrial/commercial and automotive areas. Potential parts might be high-speed and precision machinery, robotics, and structural automotive parts such as door intrusion beams, frames, engine components (push rods and connecting rods), driveshafts, and leaf springs.

## HIGH PERFORMANCE FIBERS FOR METAL MATRIX COMPOSITES

## Major Current Fibers

The family of materials classified as metal-matrix composites (MMCs) comprises a very broad range of advanced composites of great importance to both industrial and aerospace applications. However, the development and use of MMCs are still in their infancy when compared to monolithic materials or even resin-matrix composite systems. Therefore, only a handful of applications have been designed and produced, but these are illustrative of the potential of MMCs. As in the case of other composites discussed in this report, the family of metal-matrix composites is made up of many varieties of materials, which can be categorized based on their matrix composition, fabrication process, or reinforcement type. The generic listing in Table 2.2

TABLE 2.2 Advantage of PMCs

| <u>Matrix<br/>(alloy class)</u> | <u>Reinforcement<br/>Fiber</u>                                  | <u>Whisker and Particle</u>               | <u>Process</u>                      |
|---------------------------------|---|---|-------------------------------------|
| Lead                            | Glass<br>Boron<br>Carbon  |   | Cast<br>Diffusion bond              |
| Magnesium                       | Boron<br>Carbon<br>Alumina                                      | Silicon carbide<br>Boron carbide          | Cast<br>Diffusion bond<br>Extrude   |
| Aluminum                        | Glass<br>Boron<br>Steel<br>Silicon carbide<br>Carbon<br>Alumina | Silicon carbide<br>Boron carbide<br>Glass | Cast/Diffusion<br>bond/extrude      |
| Copper                          | Carbon<br>Tungsten  | Silicon carbide                           | Cast/Diffusion<br>bond/Electroplate |
| Titanium                        | Boron<br>Silicon carbide<br>Alumina                             | Beryllium                                 | Diffusion bond                      |
| Nickel                          | Boron<br>Alumina<br>Tungsten<br>Carbon                          | Alumina                                   | Cast/Diffusion<br>bond/Electroplate |

illustrates the range of possibilities, which have all been fabricated and investigated with varying degrees of success. As will be discussed in the next section, another method of classifying these composites may be based on cost.

The engineering importance of metal-matrix composites can be related to two significant advantages:

- **Properties:** The use of metals as matrices imparts important properties to the resultant composites. High matrix strength and elastic modulus impart high composite shear and transverse strength and stiffness. As an example, a boron-fiber-reinforced aluminum system exhibits transverse tensile strength equal to the unreinforced matrix and transverse stiffness twice that of the matrix. Similarly, the matrix can impart significant toughness and resistance to the operating environment resembling the characteristics of the parent metal. Metal-like thermal and electrical properties also are of importance.

- **Processing:** The ability to use traditional metal processing facilities to create at least selected metal-matrix systems is important because it brings to bear a large existing industrial capacity for component production.

On the other hand, there are also significant difficulties in the creation of metal-matrix composites. The frequently high fabrication temperatures and reactivity of many alloy matrix-fiber combinations can cause significant deterioration of properties. Similarly, the mismatch in thermal expansion between fiber and matrix can ruin composite performance on thermal cycling. Finally, the composites may differ in corrosion resistance from the parent matrix because of the composite microstructure and the difference in fiber-matrix electrochemical potential.

As indicated above, another convenient way to look at MMC systems is to consider their cost. Tables 2.3 and 2.4 are based on this approach.

Table 2.3 illustrates low-cost MMCs for industrial and aerospace applications, and Table 2.4 illustrates high-cost applications. Selective reinforcement, such as that used in Japanese automotive applications and powder metallurgical processing, can yield low-cost products. The very high performance requirements of aerospace applications have generally required the use of more costly continuous fibers and slower, more expensive processes, such as diffusion bonding.

#### *Industrial Sources: Industry Structure*

Market demand for MMCs is small and unpredictable. Therefore, few U.S. producers have been interested in developing fibers for these matrices without financial support from the DOD for a specific application.

Comparison of the status of metal-matrix composites in the United States and other countries is difficult, because the majority of the activities are still developmental and not widely publicized. However, it is known that

TABLE 2.3 Low-Cost (Aluminum-Matrix) MMCs for Industrial and Aerospace Applications

| <u>Fiber</u>   | <u>Application</u>  | <u>Fabrication Process</u> | <u>Company</u>  |
|--|---|----------------------------|---|
| Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub><br>C              | Auto diesel engines<br>Piston ring groove reinforcement         | Squeeze casting<br>—       | Toyota<br>Toyota  |
| Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub><br>(particulates) | Castings (gear boxes<br>impellers, high<br>pressure dies, etc.) | Direct chill<br>casting    | Alcan<br>Aluminum<br>Canada   |
| SiC<br>(particulates)  | Optical grade<br>(low creep) components                         | Powder<br>metallurgy       | Advanced<br>Composites<br><br>Materials<br>Corp. and<br>D W A<br><br>(CA) |
| Associates   |   |                            |   |

TABLE 2.4 Some Higher-Cost MMC Aerospace Applications

| Fiber/Matrix       | Application  |
|--------------------|--|
| B/Al; B/Ti         | Space Shuttle Orbiter fuselage: fighter aircraft engines |
| C/Al; C/MG         | Antenna mast for Hubble telescope                        |
| Particulate/SiC/Al | Various aerospace component parts                        |

foreign countries are very interested in MMCs and are trying to develop the technology. For example, British Petroleum purchased a silicon-carbide fiber capability (Sigma) and an American MMC fabricator (DWA Associates), and Alcan Aluminum of Canada purchased the Dural composites activity and has invested heavily in its expansion.

For aerospace-grade MMCs, the production applications, such as the Space Shuttle fuselage struts or satellite members, have occurred within the U.S.

aerospace industry. However, there are large developmental efforts under way in the Soviet Union, Europe, and Japan. The Soviet Union has significant efforts in at least two areas: boron-reinforced aluminum and silicon-carbide-reinforced titanium. One significant foreign development activity is proceeding within a European consortium of aerospace manufacturers who are developing titanium-matrix composites based on the British Petroleum Sigma fiber (silicon-carbide). This effort appears to be very appreciable in size, in terms of the capital and manpower resources being committed.

A second activity that is significant because of its organizational structure is Japan's metal-matrix development. This is an integrated effort between government and industry to develop both a commercial and a technical base. The first large-scale production application of MMCs was made by the Japanese in the Toyota engine piston insert. Although it is not a high-performance application, experience and confidence in production were gained.

The Japanese are committed to pursuing higher-performance MMCs as well. They have established a government/industry team, that has specific goals for developing high-temperature fibers and composites for hypersonic applications. They are also pursuing silicon-carbide-reinforced titanium and titanium aluminides as well as yarn-reinforced, thin-gauge, aluminum-matrix composites.

In summary, international investment in MMCs by both industry and government sponsorship appears to be on the rise. In addition, much of the U.S. capability in this area has been purchased by foreign companies. To date, these appear to have significantly enhanced the technology through investment, and it is unfortunate that U.S. firms have not been able to make similar commitments.

#### *Future Application Challenges*

The application needs for MMCs arise from their significant advantages over existing monolithic metals and polymer-matrix systems. Aircraft that require a lightweight structure with high stiffness or strength may have metal-matrix-composite control surfaces. For high-load applications, steel parts may be replaced with titanium-matrix composites. Future engines are probably the biggest potential application for MMCs. They require high stiffness and strength and have many parts that operate at temperatures too high for resin-matrix composites. In addition, engine parts are very sensitive to weight because of the rotating inertia, which justifies higher costs for advanced materials. Turbine parts, which operate above 500°C are currently made of superalloys. Replacement of these parts by titanium-matrix composites at half the density could reduce the weight of the engine dramatically and increase its performance.

An exciting future application of metal-matrix composites will be on air-breathing hypersonic vehicles. The national goal of demonstrating a space-capable aircraft cannot be met with traditional manufacturing processes, materials, and structural concepts. New lighter-weight materials are needed, which can take the flight loads, acoustic noise, and searing temperatures well beyond the performance of existing metals or polymer composites. This requirement, based primarily on the mission of the National Aerospace Plane

(NASP) and the above-described need for gas turbine engines, has caused considerable interest in the development of intermetallic-matrix composites. These composites constitute a subset of the more traditional MMC systems in that the matrices are ordered structures whose mechanical properties may include limited ductility over certain temperature ranges. The advantages of these systems, however, relate to their low density and high potential for use at elevated temperatures. Examples of current systems under investigation are listed in Table 2.5.

TABLE 2.5 Some Current High-Performance-Fiber Reinforced MMC Systems Under Development

| <u>Matrix Alloy</u> | <u>Reinforcing Fiber</u>                          | <u>Maximum-Use Temperature</u> |
|---------------------|---|--------------------------------|
| Aluminum            | C<br>SiC  | 300°C                          |
| Titanium            | SiC   | 500°C                          |
| Ti-Aluminides       |   |                                |
| o Alpha-2           | SiC   | >600°C                         |
| o Gamma             | TiB <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> | >800°C                         |
| Copper              | C   | 700°C                          |

*Critical Problems to be Solved for New Applications.*

In addition to availability and resource problems, there are many technical challenges remaining in the development of high-performance metal-matrix composites. Most of these involve the reinforcing fiber.

Some of the problems encountered are caused by the reaction between the matrix (metal) and the reinforcing fibers. Most MMC fabrication processes use high-temperature consolidation, which causes the metal to flow around the fibers and bond by solid-state diffusion. The majority of metals, however, are very aggressive at elevated temperatures and try to dissolve the fiber. This problem has been solved, in most cases, by developing specialized coatings for the fibers. These coatings, which are tailored for use in a specific metal matrix, are difficult and costly to develop and produce. This makes experimentation with various combinations of fibers and matrices a lengthy and expensive process. The problem is amplified because the basic understanding of the chemical, mechanical, and thermodynamic relationships in the fiber-matrix interaction are not well understood.

The recent requirements for high-temperature structures, such as for the NASP, have caused researchers to begin examining a whole new range of fiber



and matrix combinations, such as matrices of alpha-2 and gamma-based titanium alloys with fibers of titanium diboride or titanium carbide. This has resulted in a whole new set of fiber-matrix compatibility studies and development efforts that will require considerable time to carry out.

While there are many technical challenges to be overcome for MMC applications, the economic and managerial challenges are also very significant. Some measure of the problem is provided by the following comparison: sales of titanium-matrix composites in 1989 were only a few thousand pounds, while nearly 50 million pounds of titanium and several billion pounds of aluminum were produced. Therefore, a comprehensive plan to develop the basic science and production capabilities must come from something other than natural market forces.

Conclusion: Metal-matrix commercial industrial composites have the potential for large-scale applications that require a low-cost reinforcement.

Recommendation: Fibers compatible with low-cost metal-casting processes should be developed.

## HIGH PERFORMANCE FIBERS FOR CERAMIC MATRIX COMPOSITES

### Major Current Fibers and Their Properties

The addition of fibers and whiskers to ceramic matrices can result in structural composite materials that retain the important advantages of ceramics (i.e., high-temperature resistance, environmental stability, and low density) while also overcoming the drawback of brittle behavior.

A list of some of the more prominent fibers currently available for use in ceramic matrix composites (CMCs) is given in Table 2.6. In the United States CMCs have experienced serious and concentrated development only in the past 5 years. Their application as structural materials is thus, still in its infancy. Nevertheless, CMCs have many potential performance advantages that clearly indicate that within the next decade or so they will begin to see major use.

Although the brittle nature of monolithic ceramic materials has severely limited their application, it is possible to substantially increase both strength and toughness by incorporating second-phase constituents. These properties are illustrated in Figure 2.3, which compares simple flexural test load-deflection curves for unreinforced and carbon-fiber-reinforced cement composites.<sup>1</sup>

The superior thermal stability of many ceramics relative to polymers and metals makes CMCs unique for high-temperature applications. This fact, combined with the relative low density and chemical inertness of ceramics, (see Figure 2.4) make CMCs very attractive for many potential applications.

One of the major reasons that ceramics are the largest single class of materials used, despite their brittleness, is their low cost. The prospect of

TABLE 2.6 Commercially Available Fibers for the Reinforcement of CMCs

| Fiber      | Manufacturer      | Composition   | Diameter ( $\mu\text{m}$ ) | Modulus (GPa) | Strength (MPa) |
|------------|-------------------|---|----------------------------|---------------|----------------|
| NICALON    | Nippon Carbon     | Si-C-O  | 10-20                      | 195           | 2900           |
| Tyranno    | Ube               | Si-C-Ti-O   | 8-10                       | 205           | 2750           |
| Sumica     | Sumitomo Chemical | $\text{Al}_2\text{O}_3/\text{SiO}_2$                      | 10-17                      | 200           | 1500           |
| Nextel 312 | 3M                | $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{B}_2\text{O}_3$ | 8-12                       | 152           | 1725           |
| Nextel 440 | 3M                | $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{B}_2\text{O}_3$ | 10-12                      | 189           | 2110           |
| Nextel 480 | 3M                | $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{B}_2\text{O}_3$ | 10-12                      | 225           | 2285           |
| FP         | duPont            | $\text{Al}_2\text{O}_3$                                   | 20                         | 380           | 1380           |
| PRD-166    | duPont            | $\text{Al}_2\text{O}_3\text{ZrO}_2$                       | 20                         | 380           | 2108           |
| SCS-6      | Textron           | SiC on C  | 140                        | 415           | 3900           |
| Sigma      | British Petroleum | SiC on W  | 100                        | 400           | 3600           |
| Saphikon   | Saphikon, Inc.    | $\text{Al}_2\text{O}_3$                                   | 150-250                    | 350           | 2050           |
| Carbon     | Many companies    | C   | 7-12                       | 200-900       | 2700-5000      |

preserving this low cost while increasing their utility through toughening provides the opportunity for expanded CMC usage, such as in cement, concrete, bricks, and tile.

#### *Fabrication and Application*

Many approaches are currently being pursued for the fabrication and application of CMCs (see Table 2.7). Among these, however, only a few systems have reached the developmental stage, which allows them to be available for potential use. Table 2.8 shows some examples of applications of CMCs to construction, aerospace, and other industrial uses, such as cutting tools.

#### *Industrial Sources: Industry Structure*

Table 2.9 lists some of the sources prominent in the development of CMCs. Some are material suppliers from whom CMCs or CMC components can be commercially purchased, and others are developing the material for their own use, for R&D, or for potential future commercialization. The development of CMCs has been and continues to be an international endeavor. Through the success of these programs there has been a considerable increase in interest in CMCs worldwide.

Special mention should be made of the successful flight demonstration by the French company Societe Europeene de Propulsion (SEP) of its chemical vapor infiltration (CVI)-produced CMCs in advanced gas turbines. Dramatically demonstrated in flight at the 1989 Paris air show, this marks an important

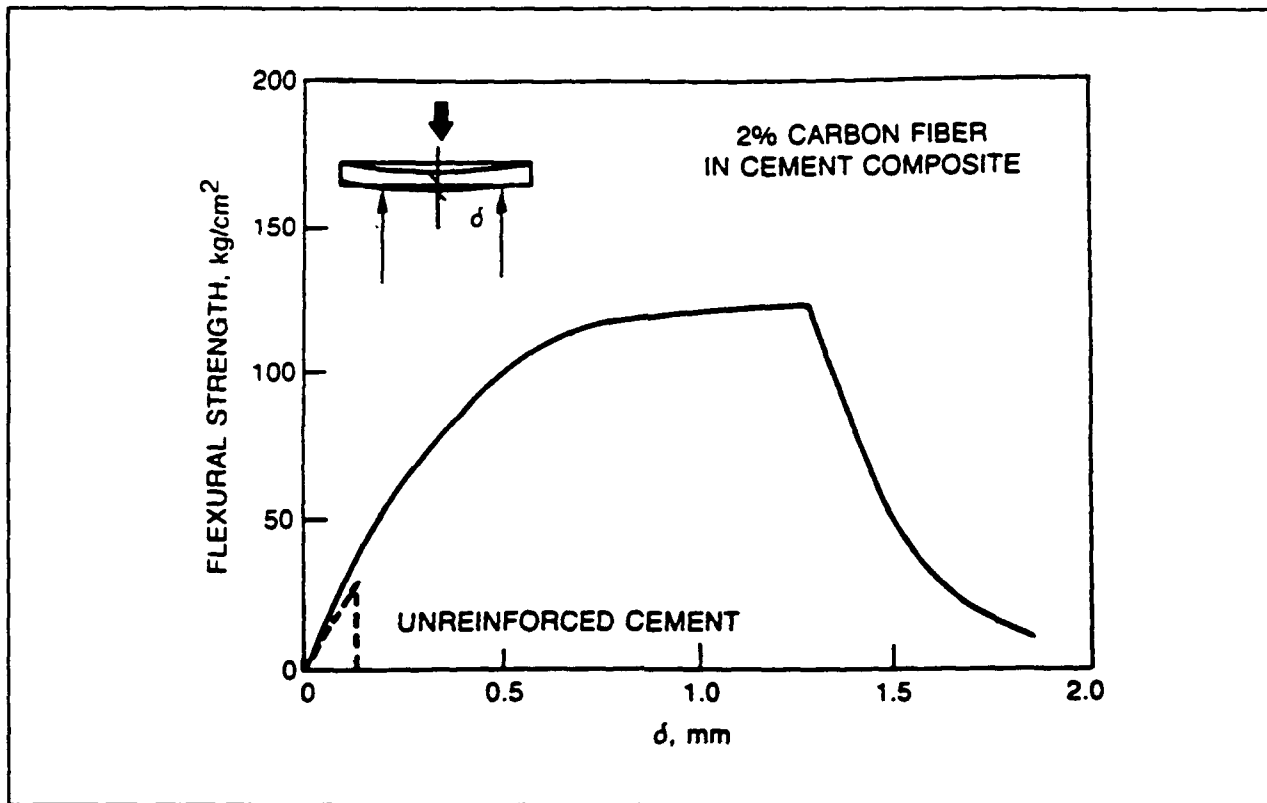


FIGURE 2.3. Comparison of bend tests for unreinforced cement and cement-matrix composites containing 2 percent chopped carbon fiber.

first that has not been duplicated by any U.S. company. The in-service experience to be gained will be of significance in enlarging the scope of the overall French program, which is extremely competitive because it encompasses all necessary aspects of composites technology, including a very active ceramic fiber development activity. A similar program does not exist in the United States. It is important to note that duPont in the United States has been licensed to use the SEP technology for making SiC-matrix composites by CVI and has made a major investment in establishing a domestic production capability. This is an important example of bringing a non-U.S.-based technology, superior to any in the United States, into this country for application.

#### Future Application Challenges

The range of future applications can be very large and can span a broad spectrum of areas. Emphasis is usually placed on the high-technology areas, but it will be clear, as demonstrated above, that construction and industrial applications are also important. Likewise, while high-temperature applications are usually emphasized, it should be noted that applications in competition with PMCs and MMCs are also possible based on other considerations, such as the superior environmental stability attainable by

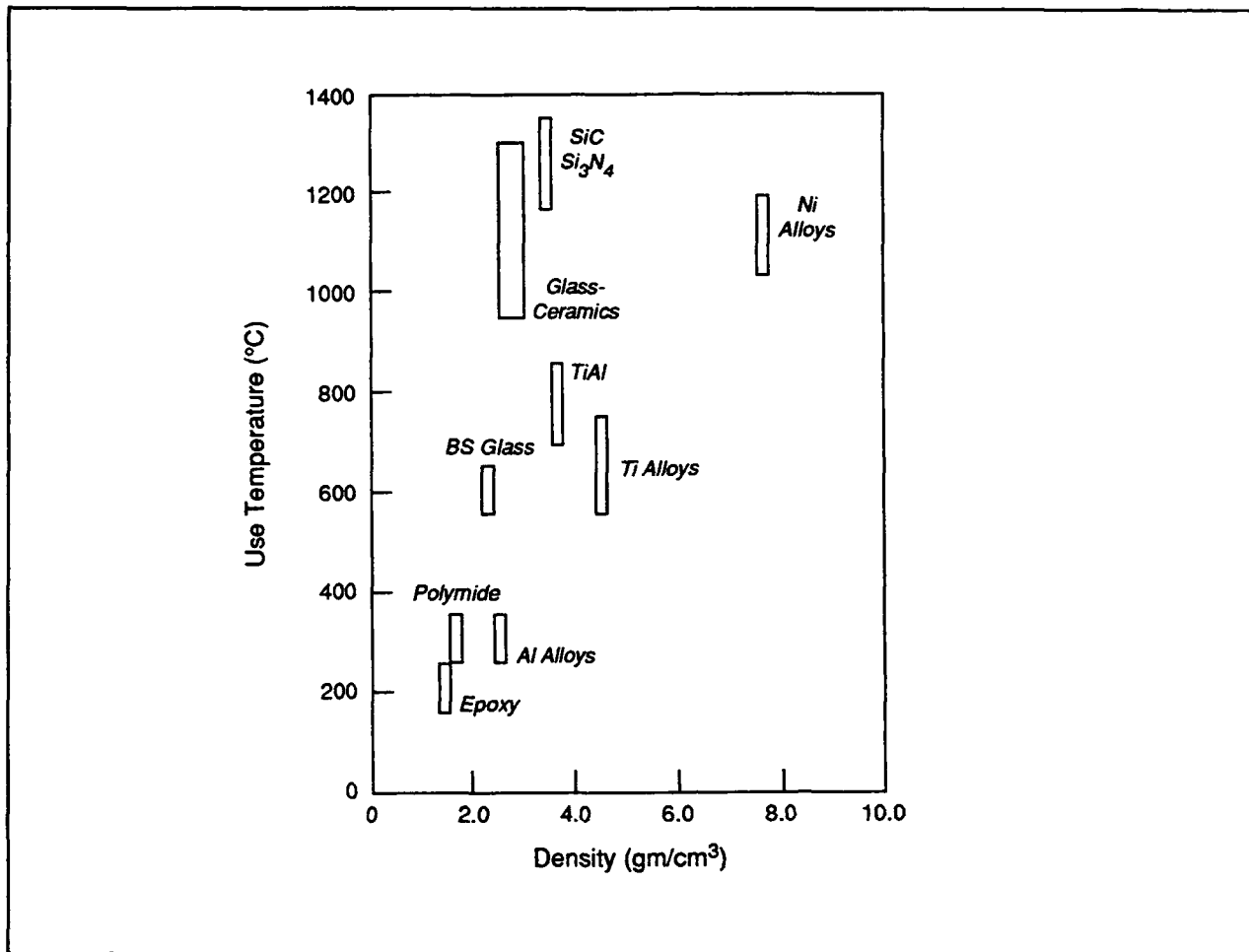


FIGURE 2.4. Densities and use temperatures of potential composite matrices.

*CMC.* A classic example of this can be found in comparing CMC candidates with aluminum or titanium. CMC materials can have significantly lower density and are competitive over the entire temperature range of performance, not just at high temperatures. The effects of environment will undoubtedly be most important in determining the successful candidate for a particular application.

The use of CMCs for space-based satellite applications is being pursued currently as part of the strategic defense initiative (SDI) program. This interest is based on the potential performance advantages of carbon-fiber-reinforced glass<sup>5</sup>. In this case there are two important areas of interest. First, space satellite structures and reflectors must remain very dimensionally stable over the orbital temperature range, they must be resistant to attack by atomic oxygen, and they must be highly damage tolerant. This last point includes mechanical damage from debris as well as thermally induced damage due to hostile threats. It is possible to incorporate all of

TABLE 2.7 Manufacturing Process for CMCs

| <u>Process</u>                                 | <u>Examples<br/>(Fiber/Matrix)</u>               |
|--|--|
| Glass powder and hot press                     | NICALON/LAS                                      |
| o Ply lay up and hot press                     | Carbon/glass                                     |
| o Matrix transfer mold                         | FP alumina/glass                                 |
| o Injection mold                               | Nextel/glass                                     |
| Chemical vapor infiltration                    | NICALON/SiC                                      |
| o Infiltrate prewoven structures               | Carbon/SiC                                       |
|  | Nextel/glass                                     |
| Polymer conversion                             | NICALON/SiC                                      |
| o Infiltrate and pyrolyze                      |  |
| Sol-Gel  | Carbon/glass                                     |
| o Infiltrate and pyrolyze                      | Nextel/mullite                                   |
| Ceramic powder and hot press, sinter           |  |
| o Ply lay up and hot press                     | SiC/Si <sub>3</sub> N <sub>4</sub>               |
| o Blended constituents and hot press or sinter | SiC <sub>w</sub> /Si <sub>3</sub> N <sub>4</sub> |
|  | SiC <sub>w</sub> /Al <sub>2</sub> O <sub>3</sub> |
| Cementitious processing                        | Carbon/cement                                    |
|  | Glass/cement                                     |
|  | Steel/cement                                     |
| Liquid metal oxidation (lanxide)               | NICALON/Al <sub>2</sub> O <sub>3</sub>           |
|  | SiC <sub>w</sub> /Al <sub>2</sub> O <sub>3</sub> |
| Liquid infiltration                            | SiC/SiC (Si)                                     |
| Reaction forming                               | SiC/Si <sub>3</sub> N <sub>4</sub>               |

these qualities in CMC systems. One example of this is the high-performance mirrors produced from carbon-fiber-reinforced glass for use in laser systems.<sup>6</sup>

The potential use of CMCs at very high temperatures can be illustrated by comparing available tensile strength data of several composites with the strength of currently used superalloys (see Figure 2.5). The comparison does not include the effects of environment since the composites were tested in inert atmosphere. The SiC fiber used for these composites was Nicalon®. All

TABLE 2.8 Some Applications of CMCs

| <u>Application</u> | <u>Fiber or Composite</u>                  | <u>Property Enhancement or Product</u>            |
|--------------------|--|---|
| Construction       | 1-3 volume percent chopped fiber in cement | Enhanced flexural strength; light-weight concrete |
| Industrial         | SiC in Al <sub>2</sub> O <sub>3</sub>      | Improved cutting tool material                    |
| Aerospace          | C, SiC                                     | Gas turbine engine parts                          |

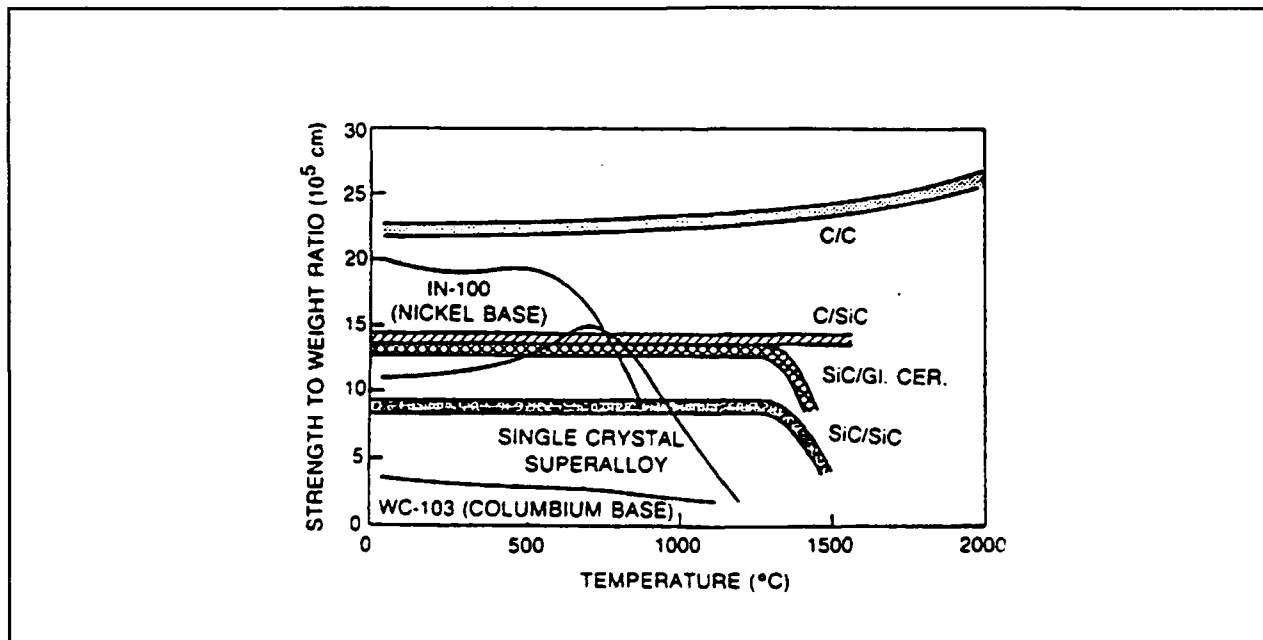


FIGURE 2.5. Specific strength comparison of high-temperature metal alloys and advanced composites (two-dimensional fiber-matrix).

composites were bidirectionally reinforced. The use of carbon fibers provides the highest level of performance owing to carbon fiber's unique low density, high strength, and retention of strength to the highest possible temperature.

TABLE 2.9 Some Current Sources of CMCs

| <u>Matrix Fabrication Process</u> | <u>Source</u>   |
|-----------------------------------|---|
| Chemical vapor infiltration       | SEP<br>duPont<br>Amercom<br>Refractory Composites<br>Oak Ridge National Laboratories<br>General Atomics<br>3M |
| Glass/glass ceramic               | Corning Glass<br>United Technologies Corp.<br>Nippon Carbon Co.   |
| Hot pressed and sintered          | Greenleaf<br>Advanced Composite Materials<br>Oak Ridge National Laboratories<br>GTE<br>Norton<br>Textron      |
| Polymer conversion                | Kaiser Aerotech<br>General Atomics  |
| Sol-Gel                           | Babcock & Wilcox<br>Pratt & Whitney   |
| Reaction forming                  | Lanxide<br>General Electric   |

Although the Nicalon<sup>®</sup> fiber tensile strength is expected to decrease significantly at about 1300°C, it is notable that composite strength is maintained even to this temperature. The strength and stability properties of newer versions of Nicalon<sup>®8</sup> as well as these of new fibers such as Tyranno<sup>9</sup> indicate the potential to increase maximum-use temperatures in the future. Also, coating approaches are currently under development to allow long-term use of the C/SiC and SiC/SiC composites in oxidizing environments.

#### *Critical Problems to Be Solved for New Applications*

Being the newest class of advanced high-performance composites, the full range of potential applicability of CMCs has not yet been realized. While the more obvious high-temperature potential of these systems has formed the primary focus for research, the potential for use at lower temperatures should be investigated.

Specific strength comparison of high temperature metal alloys and advanced composites (two-dimensional fiber-matrix) should also be explored. The future widespread use of CMCs must begin with prudent identification of applications that will help to develop a sound basis for their reliable use.

This may mean beginning with emergent CMC systems and applications that do not require either the highest level of structural performance or maximum temperature capability, nor that are optimum in their payoff, but instead serve a useful purpose, are cost effective, and give the opportunity to demonstrate reliable production methods, non-destructive evaluation (NDE) techniques, and design principles. This approach would allow a broader range of applications to be found for CMCs, and it would offer the potential to further support the overall technology base.

#### HIGH PERFORMANCE FIBERS FOR CARBON-CARBON COMPOSITES

Carbon-carbon (C-C) composites are structures in which both the matrix and the reinforcement are carbon. They offer many advantages in high-temperature applications over composites fabricated with other matrix materials. The unique high-temperature mechanical property retention of C-C composites (in excess of 2200°C) and their low density (1.5 to 2.0 g/cc) make them useful at high temperatures (i.e., above 1350°C in some cases and above 1700°C for short-time, limited-use application). For continuously reinforced C-C composites, it is the mechanical properties of the carbon-graphite fibers that dominate the C-C composite properties, and it is the high-temperature capability of the carbon matrix that allows one to take advantage of the fiber properties at elevated temperatures, where most metal matrices have melted or polymer matrices have decomposed or melted.

The major drawback of C-C composites is lack of oxidation resistance. Carbon's oxidation rate increases dramatically above 600°C, and unless an oxygen barrier or inhibitor is applied to the C-C composite or its constituents, operational time above this temperature is limited. Another disadvantage of high-performance C-C composites is fabrication cost, which is a result of the high fiber cost, the long processing times, the many fabrication steps needed to achieve the desired composite properties, and the expense associated with the use of high-temperature processing equipment. However, in many applications where C-C composites are considered for use, government specifications dictate the use of expensive manufacturing methods or preclude the use of any other matrix.

A continuous fiber C-C composite is fabricated by first forming a "preform" of carbon-graphite fibers either by weaving a fabric that is used to build up a structural shape (involutes, rolled fabric, pierced fabric, etc.), by weaving straight fibers in multidimensions, or by braiding. This preform is then densified; that is carbon is added to the interstices of the fiber preform to become the matrix of the composite. Formation of the carbon matrix can be accomplished by a number of methods: conversion of liquid resin or liquid pitch precursors, gaseous or CVI, or combinations of these to achieve desired physical properties. Discontinuously reinforced C-C may be fabricated by starting with a carbon fiber felt and densifying by CVI or by mixing carbon fibers or whiskers in a carbon-forming precursor and then pyrolyzing and graphitizing.



## Major Uses and Current Systems

The major uses and systems employing C-C composites are listed in Table 2.10. As shown, military and aerospace requirements dominate high-performance applications, where structural and thermal properties are of crucial importance. The largest volume application, to commercial aircraft brakes, does not require high performance; this is also true of the application to furnace insulation material. For these applications relatively inexpensive fiber components, such as chopped or discontinuous fibers, are adequate.

TABLE 2.10 Major Uses of C-C Composites

| <u>Military/Aerospace</u>      | <u>Commercial</u>           |
|--------------------------------|-----------------------------|
| Rocket nozzles                 | Brakes for aircraft, racing |
| Nosecones for reentry vehicles | cars                        |
| Heat Shields                   | High temperature furnace    |
| Brakes for aircraft            | insulation                  |

## Future Application Challenges

C-C composites can be expected to consistently outperform other materials wherever there is a high-temperature thermostructural requirement if oxidation of the composite is precluded. One of the biggest impact areas of C-C composites is in gas turbine engines.

The use of C-C composites in hypersonic vehicles will continue, but more benefits can be gained through incorporation of the newly developed, high thermal conductivity, pitch-based carbon fibers. Hypersonic vehicles will need C-C composite leading edge and skin materials to withstand the extreme aerothermal heating of the atmosphere. Additionally, because structural weight fraction requirements are so stringent, the C-C composites must be structurally and thermally functional. Very thin components (i.e., 10- 20-mil-thick panels) will be needed with high modulus and strength to carry airframe loads. High composite thermal conductivity will be required to transfer aerodynamic heat to a sink, so that vehicle surface temperatures can be kept to a minimum consistent with the maximum operational temperature of oxidation-resistant coatings.

The high temperature, strength, and toughness capabilities of C-C composites make them extremely attractive for future military applications where laser weapons might be encountered. The high cost of these composites precludes use in many applications, but in very high value platforms, as in space, where survivable structures are required, C-C composite costs are justified.

For spacecraft applications, C-C composites have attractive properties that will enable them to trade off well even if hostile-threat survival is not a requirement. Three types of spacecraft components are available for C-C

composite insertions: structural, dimensionally stable, and thermal management components. The relatively low carbon-matrix modulus of elasticity causes very little matrix contribution to the C-C composite thermal expansion coefficient, and thus a zero or slightly negative thermal expansion coefficient of the composite can be obtained by using carbon fibers with these same properties.

It has been shown that highly graphitic fibers are resistant to shrinkage under intense neutron radiation. This attribute, together with other properties of high-temperature strength, toughness, and low nuclear cross section, makes highly graphitized C-C composites applicable for nuclear power plant applications.

Applications that could potentially be exploited for economic considerations are in high-temperature processing of materials. Some examples include containers for molten metal, high-temperature bearings in steel mills and chemical processing plants.

Oxidation is the most critical problem to overcome if C-C composites are to be widely used in a variety of applications. Composite surface coatings can provide protection, but to provide for a more gradual degradation in the performance of the composite in the event of a breach in the coating, internal oxidation resistance must be designed into the C-C composite substrate. The high cost of C-C composites is also a major issue and must be addressed on many fronts. The major contributors to the high costs are fiber cost, preforming costs, and densification costs. The technical issues involved are discussed further in Chapter 4.

#### HIGH PERFORMANCE FIBERS FOR NONSTRUCTURAL APPLICATIONS

As pointed out earlier, composites—especially advanced composites—are used primarily in structural and semistructural applications for which the dominant considerations are mechanical properties, such as stiffness, static strength, and resistance to fatigue, creep, and creep rupture. However, there are many applications for which other physical properties, alone or in combination with mechanical properties, dominate the selection process. These physical properties include electrical conductivity, thermal conductivity, coefficient of thermal expansion (CTE), dielectric properties and magnetic characteristics. Although there are currently many applications for which these properties are critical factors in the choice of materials, their unique properties in composites have not been fully exploited. This chapter considers current and potential applications for which nonstructural physical properties are key requirements and examines the needs for new or improved fibers to exploit these properties.

## Major Uses: Current and Projected

### *Electrical and Electromagnetic Properties*

The most widely used synthetic composite reinforcement is E-glass fiber, which was developed for electrical applications. Although the major uses of E-glass at the present time are in structural and semistructural applications, E-glass-reinforced polymers are widely used in applications where electrical insulation is required. Examples include generators, motors, printed circuit boards (PCBs), and industrial ladders. In these applications, design requirements include a physical property, and electrical resistivity as well as mechanical properties. Dielectric strength is another important electrical property, especially for high-voltage applications.

Low dielectric constant and loss tangent are key design requirements in applications where the transmission of electromagnetic energy is important. The most common example is probably the radome, which is widely used in airborne and land-based radar and communications systems. Reinforcements here are typically E-glass, quartz, and aramide fibers. Alumina fibers are used in high-temperature ceramic-matrix composite radomes.

In some applications it is desirable to have materials that absorb electromagnetic energy. This can be achieved by using polymers or ceramics reinforced with fibers whose electromagnetic properties are tailored for the purpose by varying chemical composition, structure, or both. For example, the electrical conductivity of carbon fibers can be varied over many orders of magnitude. Therefore, they are used in applications ranging from static dissipation to EMI and RFI shielding. One problem is the stability of carbon fiber electromagnetic properties in some property ranges. Other fibers used for their electromagnetic properties are a variety of oxides and silicon carbide. Silicon nitride fibers are under development for this purpose. At this time it is often the case that tailoring electromagnetic properties is achieved at the cost of reduced strength, modulus, or both.

Fiber-reinforced materials play a key role in current applications for which tailored electromagnetic properties are important. This undoubtedly will continue for the foreseeable future. With present materials, there is often a penalty in reduced structural properties when reinforcements are selected for their electromagnetic properties. Development of new or improved fibers with good structural characteristics and tailorable electromagnetic properties is highly desirable.

The low density of carbon fibers makes them attractive candidates for electrical conductors in applications for which weight is critical. Aircraft and spacecraft are obvious examples. Another possible use is in transmission lines. Here, their high specific stiffness and strength would permit support towers to be placed farther apart, reducing construction costs. The high-temperature creep resistance of carbon fibers is another advantage over conventional metal conductors. Although carbon fibers are electrically conductive, their resistivity is much higher than that of copper. This has been overcome, experimentally, by intercalation. However, an equally viable solution may be to use carbon fiber to carry the load of the transmission line

and traditional aluminum cable to conduct power—a composite transmission line.

### *Thermal Properties*

It is a remarkable fact that a number of carbon fibers have extremely high axial thermal conductivities. For example, experimental vapor-grown fibers have been produced with thermal conductivities approaching 2000 W/m K, five times that of copper. Commercial pitch-based ultrahigh modulus carbon fibers are available with reported conductivities as high as 700 W/m K. These relatively new materials have considerable potential in applications where thermal control is important. Examples include spacecraft radiators, electronic packaging, and high-temperature supersonic aircraft structures, such as those of the National Aerospace Plane (NASP). It should be noted that carbon fibers are strongly anisotropic, and their transverse conductivities are about an order of magnitude lower than the axial. This can be a serious limitation in applications where through-thickness conductivity is important.

Conversely, fiber-reinforced matrix composites also are used in applications where low thermal conductivity is a major consideration. For example, E-glass/epoxy straps are used to support and thermally isolate cryogenic tanks used to store helium in nuclear magnetic resonance instruments.

One of the characteristics of molecularly oriented fibers (either carbon or polymeric) is a low and controllable axial coefficient of expansion. This has led to their use in applications where dimensional stability is a key design requirement. The high specific stiffnesses and strengths of these materials contribute to their attractiveness in numerous spacecraft structures, such as the Hubble Space Telescope and antenna support towers. Add to these features electrical conductivity and it is not surprising that carbon fiber-reinforced polymers are the materials of choice for aircraft and spacecraft antenna reflectors.

Requirements for future avionics systems are exceeding the capabilities of conventional low-expansivity monolithic metals used in electronic packaging, such as Kovar, Invar and molybdenum. Low CTE is required to match those of semiconductors and ceramic substrates. Applications include microwave packages, microelectronic packages, and heat sinks. If there is a CTE mismatch, severe thermal stresses can arise, causing mechanical failures. Key requirements, in addition to low CTE, are high thermal conductivity and low density. There are no monolithic metals possessing all three characteristics. The development of lightweight, low-cost, microwave packages may well be an enabling technology for aircraft and spacecraft large phased array antennas, which may use thousands of elements.

The high-temperature resistance of alumina-boria-silica fibers has led to their use in a limited number of aircraft firewall structures.<sup>2</sup> Ship structures are other potential applications. One of the most visible examples of a composite designed for nonstructural uses at the present time is the thermal shield of the Space Shuttle,<sup>1</sup> with combinations of materials designed

to protect against temperatures exceeding 2000°F that are generated during reentry.

Industrial furnaces use nonstructural fibrous or fiber-reinforced composites, where the principal use is based on thermal insulation properties. Such products are available as boards or mats with structural properties that may be just sufficient to permit handling during installation. Flexible composite insulation such as blankets of staple fiber fill that is quilted between woven fabric of ceramic fibers stitched with high temperature ceramic thread may be attached to furnace walls or suspended like curtains.

#### *Chemical Properties: Corrosion Resistance*

Relatively recent work on fiber-reinforced silicon carbide ceramics has shown promise for heat exchangers, furnace tubes, regenerators, nozzles, and other components that may be required to resist thermal shock and corrosive gases at high temperatures for extended periods of time. The ceramic composite type most frequently cited in recent presentations and publications is that prepared by the application of silicon carbide by chemical vapor deposition and chemical vapor infiltration on graphite, carbon, oxide, and silicon carbide textiles.<sup>3-5</sup> Such composites comprising NEXTEL 312, NEXTEL 440, Nicalon®, and carbon felt have survived combustion tests to 1400°C for 800 hours or longer,<sup>3</sup> and tests in corrosive waste gas from a secondary aluminum remelt furnace indicated that plate-type heat exchangers comprising silicon carbide reinforced by NEXTEL or Nicalon fibers could be designed to recover waste heat from corrosive or fouling flue gases from industrial furnaces.<sup>4</sup>

#### *Cutting Tools*

A novel application for ceramic composites that are toughened and strengthened using whiskers is in cutting tools. A specific example of this is the silicon carbide whisker-reinforced alumina matrix composite (WG-300) developed by the Greenleaf Corporation.<sup>6</sup> This new tool is reported to be capable of operating at surface cutting speeds up to about 10 times as fast as tungsten carbide and cobalt cermet tools. The superior performance is apparently related to the higher-temperature properties of the whisker-reinforced ceramic.

#### *Piezoelectric Sensing and Actuating*

Piezoelectric materials contract when subjected to electrical currents and, conversely, emit electrical signals when strained. These properties make them useful both as actuators and sensors. Piezoelectric fibers have been produced on an experimental basis. Potentially, they could be incorporated in various matrix materials to function as sensors, measuring strain, and to produce "active" structures, in effect, artificial muscles. Piezoelectric materials have been used as both sensors and actuators to provide active damping.

Large space structures, such as those for space-based radars, are likely to require some form of active control to meet deflection requirements.

Deformation sensors will also be required. It has been demonstrated that piezoelectric materials, in the form of films or plates, can perform these functions. Piezoelectric fibers potentially could more easily be incorporated into complex structures and could have reliability advantages over brittle ceramics in plate form. Piezoelectric fiber-reinforced composites also could have major benefits in detecting underwater acousting waves and minimizing reflected signals. It is highly likely that numerous other applications would emerge for this type of reinforcement. Reconfigurable aerodynamic surfaces is one possible example.

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### 3

## Fiber-Forming Processes: Current and Potential Methods

### INTRODUCTION

This chapter addresses the processes by which high-performance fibers are formed, with emphasis on those technologies that have been most broadly successful. The technologies include

- Polymer fibers.
- Pyrolytic conversion of precursor fibers.
- Chemical conversion of precursor fibers.
- Fibers produced by chemical vapor deposition.
- Single crystal fibers.

Also included is the important technology associated with the coating of fibers, a technology that allows chemical and physical tailoring of the fiber surface.

The processes for converting bulk materials into fibers, while specific to the desired end product, have a series of elements in common. These include

- Conversion of the room-temperature solid to a low-viscosity (up to  $10^4$  poise) melt or solution.
- Passing the filtered solution through a plate of holes (spinnerette) to form fibers.
- Solidifying the fiber over a distance of centimeters to meters under conditions of controlled temperature, stress, and mass transfer.

If the process begins with a stable melt, the process is termed "melt spinning." Solution spinning with high-volatility solvents that may be flashed off during solidification is termed "dry spinning." Conversion of solutions in low-volatility (high boiling point) solvents to fiber, requiring filament coagulation by exchanging solvent for nonsolvent, is termed "wet spinning." These processes are illustrated in Figure 3.1.

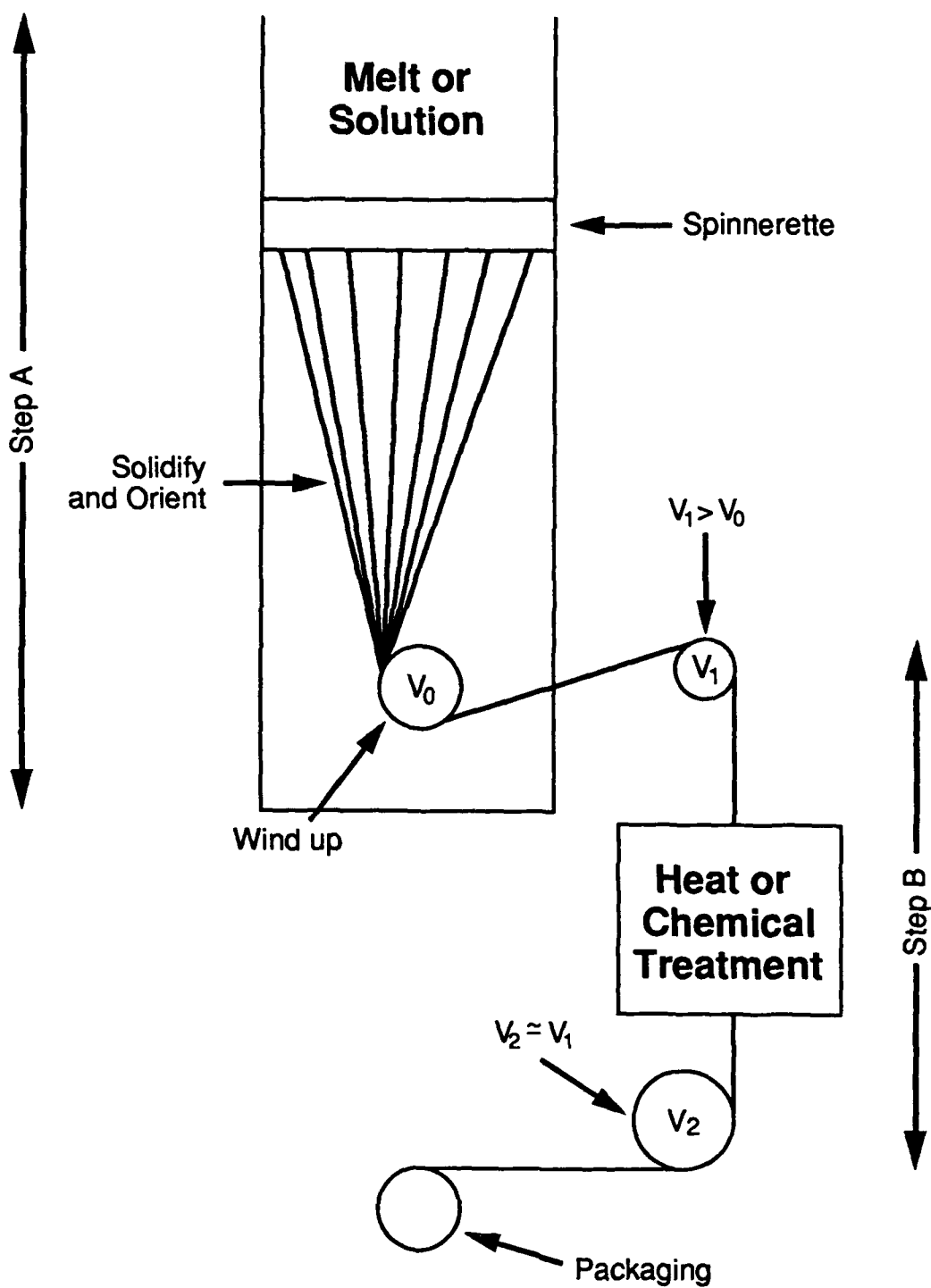


FIGURE 3.1 General processing steps for converting bulk materials to fibers.



Important variations on this theme include removal of the spinnerette from the wet spinning coagulation bath (allowing separate control of spinning and coagulation temperatures) necessary for the spinning of many lyotropic polymer systems (aramid, polyphenylene polybisbenzoxazole [PBO]) (dry jet wet spinning); and the spinning of low-concentration solution to minimize chain entanglements in the resulting fiber (gel spinning). Depending on the conditions chosen, filaments may be molecularly oriented or disoriented as spun. Additional orientation may be imparted through "drawing" processes where the molecules comprising the fibers are elongated at a rate faster than their relaxation time. Heat may be applied to yarns to increase morphological stability through controlled crystallization and/or molecular relaxation processes. Finally, chemistry through the application of heat, pressure (vacuum), or reactants may be utilized as a separate step, or in conjunction with the process steps, to convert "precursor" fibers to the desired final composition. In the ensuing portions of this chapter, processing technologies that are key to the formation of important high-performance fibers critically analyzed.

## PROCESSES TO FORM POLYMERIC ORGANIC FIBERS

### Introduction

The technical concepts behind the processing of ultrahigh-strength, (200–500 Ksi), ultrahigh-modulus (greater than 7 Msi) polymeric organic fibers differ from those for inorganic and metallic fibers and are related to the one-dimensional nature of polymeric molecular chains. To make a fiber that takes maximum advantage of the strength of the interatomic forces (covalent bonding) in the polymer, the molecules must be extended and oriented parallel to the axis of the fiber.

The commercial processes for high-strength, high-modulus fibers are based on two physical concepts: melt or dry jet wet spinning from a nematic liquid crystalline phase in which the already rod-like molecules are uniaxially ordered, and melt or gel spinning and drawing of conventional, random-coil polymers under conditions that permit extremely high elongational forces (high draw ratios) to mechanically elongate and orient the component molecules (cf. Figure 3.1).

The resulting highly oriented morphologies yield moduli that approach the theoretical. However, the relatively high strengths achieved are far (10x) from theory, offering potential for further development. These fibers are highly anisotropic, with lateral tensile properties up to two orders of magnitude lower than axial. This results in some inherent performance losses, most notably in compressive properties.

## Technical Description

### *Spinning of Liquid Crystalline Solutions*

The first commercial high-performance organic fiber, developed by the duPont Company from poly(paraphenylene) terephthalamide, under the Kevlar trademark, was spun from a nematic (liquid crystalline) solution. In a nematic phase the individual rod-like molecules are oriented parallel to their nearest neighbors. The parallel orientation exists over a correlation volume of micrometer dimensions. The elongational force field during the spinning process orients these volumes in the direction of flow. When the initially extruded fiber is fixed by extraction of the solvent, the molecules solidify in a form that places the strong molecular chains parallel to the fiber. In addition to the aramids, rigid, para-oriented, aromatic heterocyclic polymers (e.g., poly(benzobisoxazole) [PBO's]), are of greatest importance.

The cost of polymeric fibers is dependent on the cost of the starting materials and the complexity of the polymerization and conversion processes. Monomers capable of polymerization to required molecular weights must be extremely pure. The necessary steps to achieve this can add significantly to the cost and greatly complicate scale-up to commercial levels.

PBO is synthesized from expensive monomers in corrosive acid solvents such as methyl sulfonic or polyphosphonic acid. A related polymer with similar expensive monomers is the corresponding benzthiazole. The commercial aramid fiber from poly(paraphenylene terephthalamide) (PPD-T) is synthesized in amide solvents such as N-methylpyrrolidone by the condensation of p-phenylene diamine and terephthaloyl chloride. The finished polymer is washed to remove the solvent, and the equipment required for the mixing and isolation makes this an expensive process. Both aramids and the aromatic heterocyclics are redissolved and converted to highly oriented fiber through dry jet wet spinning (cf. Figure 3.1).

Aramid and PBO fibers are characterized by use temperatures up to about 250°C and by chemical inertness. The H-bonding potential to the aramids leads to moisture sensitivity with consequent property reductions under humid conditions.

### *Spinning of Liquid Crystalline Melts*

The majority of polymers in this class are aromatic copolyesters that have been previously commercialized as molding resins. Their advantage is the inherently lower cost of melt spinning, which avoids dissolution and solvent recovery steps. Melt spinning has the potential for much higher spinning rates, with a consequent decrease in capital investment per output.

The first commercial product to make its appearance is the fiber Vectran, by Hoechst Celanese and the Kuraray Company. This product's advantages include very high cut resistance (up to eight times that of the aramids) and excellent hydrolytic stability. Tensile properties at room temperature are similar to those of Kevlar® fibers but decrease with

increasing temperature. Use temperatures are intermediate between Kevlar® and polyethylene, 150° to 200°C depending on composition.

### *Gel Spinning*

High molecular weight linear polyethylene is gel spun commercially (see Introduction) with the resulting fiber being drawn to very high (20-100) draw ratios. The elongational forces cause the molecular chains to be extended and highly oriented in the fiber direction, resulting in high levels of tensile modulus and tensile strength. The solvent recovery aspect of the process and the controlled low-speed drawing increase the cost of the fiber to a level comparable to other high-strength fibers, despite the low polymer cost. Performance problems inherent in highly oriented polyethylene fibers include low-use temperature (<100°C) and creep.

### *"Normal" Solution Spinning*

Spinning of a normal isotropic (nonliquid crystalline) solution with subsequent drawing of the fiber to induce orientation can be accomplished with certain rigid molecules. Teijin has commercialized an aramid (Technora) that is a polymer of paraphenylene diamine, 4,4"-diamino diphenylether, and terephthalic acid. The fiber, after removal of the amide (N-methylpyrrolidone)/LiCl solvent, is drawn at 485°C.

### **Technical Future**

A major class of polymers with demonstrated fiber potential but no commercial product yet is the polyimides. Two Japanese companies (Ube and Toray) have announced the manufacture of fibers based on polyimides with tenacities of about 20 gpd. It is unlikely that new spinning processes will be applied to high modulus fiber production. However, the postheating processes that have been shown to improve fiber properties are poorly understood. Better understanding of these processes could lead to improved fibers. The cost of the additional step will remain a factor.

Research on the orientation of molecules in elongational and shear fields could lead to incremental but significant improvements in tenacity and modulus. Research on fiber physics, which could lead to commercially important discoveries, is not being done at an appropriate level by industry and only at a very few university laboratories.

Rheological and morphological studies have the ultimate potential of finding processes to form high-strength fibers from commodity polymers other than polyethylene. High-strength nylon or conventional polyester (polyethylene terephthalate) fibers made by a melt process could be the first high-strength fibers with prices compatible with commercial ground transportation applications and land- and marine-based applications.

Improved low-cost routes to monomers for liquid crystalline melts, or different low-cost monomers for the same polymers, could have significant commercial impact.

No process variable (other than, perhaps, molecular cross linkage) is likely to significantly improve the tendency toward compressive failure in these highly oriented materials. Process parameters are also unable to affect use temperatures, which will remain in a range well below those of ceramics.

The application of blend concepts has been exploited to a relatively small extent. The field of engineering resins has demonstrated the potential of blending to result in order-of-magnitude property changes.

The commercially announced fibers from liquid crystalline melts illustrate the strong Japanese effort toward development of fibers discovered in the United States. This reflects the unwillingness of American industry to commercially develop new materials with a limited current market.

Although industry is doing little fundamental research on organic fibers, development in general will be handled by industry more effectively than for the other fibers discussed in this report because the organics have a broader commercial market. This indicates that limited government resources should be applied to the more specialized inorganics.

## FIBER FORMATION BY PYROLYTIC CONVERSION OF PRECURSOR FIBERS

### Introduction

The use of precursors that can be pyrolyzed to form continuous inorganic filaments has provided a route to the manufacture of synthetic inorganic fibers of many different compositions. The precursor materials include polymers, concentrated salt solutions that may behave like polymeric materials, polymer-modified solutions and slurries, and sol-gel systems. Polymeric precursors are used for the fabrication of continuous nonoxide filaments such as carbon, graphite, and silicon carbide (SiC). Oxide fibers are produced from all of the precursor types listed above.

Since the rheological properties necessary for spinning continuous filaments at high speed are provided by the polymeric-type material present in the fiber-forming precursor composition, spinability of the final fiber composition in its fused form is not a necessary property, as it is in the forming of traditional glass filaments. Therefore, materials such as aluminum oxide ( $\text{Al}_2\text{O}_3$ ) or zirconium oxide ( $\text{ZrO}_2$ ) and many others may be prepared in fiber form, even though the properties of their liquid phases would not normally permit fiber spinning at any practical rate. Similarly, fibers of materials not generally considered to melt, such as carbon (C) and SiC, are also prepared by this technology. Polymeric materials may embody in their composition all of the precursor components of the final solid inorganic, such as SiC or C, or they may be present principally for their contribution to fiberizing properties. In the latter case, the polymer may be completely fugitive, while the actual fiber components exist in the precursor formulation as decomposable salt compounds or as colloids added as particles or compatible sols such as aqua sols.<sup>1</sup> Thus, formation of the inorganic fiber precursor (or organic in the case of carbon fibers) involves spinning melted polymeric

precursors, viscous polymeric solutions, or mixtures of polymers, salt solutions, and colloids. Regardless of the precursor used, the principal common steps for the fabrication of fibers with polymeric precursor systems are as shown in Figure 3.2.

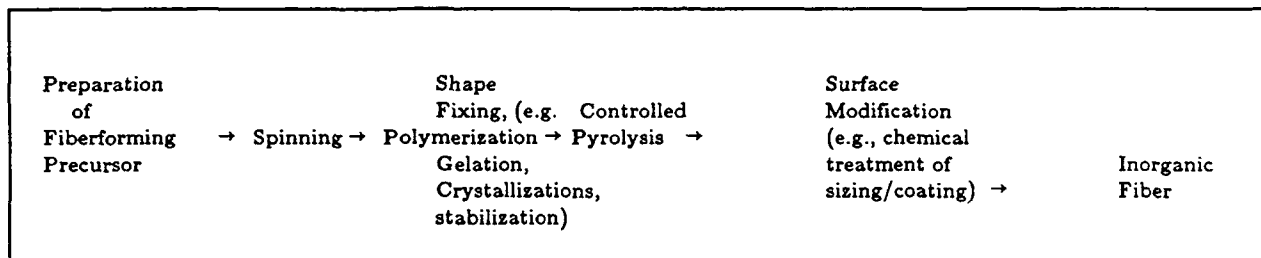


FIGURE 3.2 Simplified flowsheet for precursor pyrolysis processes.

An especially important feature of the precursor pyrolysis process, in addition to its versatility in the preparation of fibers over a wide range of compositions, is the low temperatures (350°C or lower) used for precursor fiber spinning. Despite the straightforward flowsheet of Figure 3.2, it is important to realize that precise control of conditions in each step is required for the fabrication of filaments with optimum properties. Since the pyrolysis step may involve the decomposition and removal of up to 50 percent or more of the polymeric precursor fiber, it becomes obvious that careful control at this point is extremely critical to ensure that fiber defects are minimized or that the fiber even survives this part of the process. Control at this point will include factors such as the atmosphere, temperature, and rate of temperature increase, it being necessary to control rates of decomposition and removal of volatile products as well as rates of reaction of residual precursor components of the final fiber composition. The specific details for the fabrication of fibers vary according to the composition of the final inorganic fiber and precursors used for their preparation.

The major portion of development work on inorganic fibers via the pyrolytic conversion of precursor fibers has been done since 1960. The review by Bracke et al.<sup>2</sup> provides a useful summary of the state of the art on inorganic fibers in patents and other publications up to 1984. More complete details on processing, current status, performance, and needs in the area of high-performance synthetic fibers are provided in the following sections on nonoxide and oxide fibers.

### Carbon Fibers

Even though high-performance carbon fibers were first introduced in the 1960s, the physical properties of these reinforcing fibers have improved dramatically over the past decade. This can be attributed to three developments: significant improvements in both quality and performance of the precursor fiber, a substantial increase in worldwide production capacity and the process improvements resulting from this gain in production experience, and a strong push on the part of the United States and Western European aerospace industry for high-performance carbon-based reinforcing fibers.

There are three types of precursors used on a commercial basis to manufacture carbon fibers: rayon, polyacrylonitrile (PAN), and pitch. Rayon, the raw material used for the first high-performance carbon fibers, was the dominant precursor material in the 1960s and early 1970s. However, because of its low carbon yield (20–30 percent), high processing cost, and limited physical properties, today rayon precursor is used for less than 1 percent of commercial carbon fibers. At the present time, North American Rayon is the U.S. supplier of rayon precursor, and Amoco Performance Products is the only U.S. supplier of rayon-based carbon fiber. Use of rayon-based fiber is primarily limited to C-C ablative shields. Since PAN and pitch are used as the precursor for over 99 percent of today's commercial carbon fibers, this discussion will concentrate on the strengths and limitations of the carbon fibers produced from these feedstocks. Noncontinuous carbon fibers have also been made on a developmental basis from a radically different process that does not use polymeric precursors. This process, often referred to as vapor grown carbon fiber, involves the combination of a hydrocarbon vapor with a catalyst source and hydrogen. A discussion of its process is included in the section on whisker-like materials.

#### *PAN-based Carbon Fibers*

Technical Description and Present Status. PAN-based carbon fibers are derived from polyacrylonitrile or acrylic copolymers. Normally, a solution of the polymer is either wet or dry spun into PAN precursor fibers that are ultimately converted into carbon fibers. Figure 3.3 gives a flow diagram for the process, which is well documented in the literature.<sup>1</sup> The precursor fibers used by the major PAN-based carbon fiber suppliers differ significantly from the acrylic fibers used for textile acrylic apparel and industrial applications. PAN precursor fibers have fewer filaments per tow stage, a higher level of purity, smaller filament diameter, and higher acrylonitrile (AN) content (i.e., normally greater than 90 percent AN) than fibers used in textile applications. Also, the polymer composition and molecular weight must be modified to produce the desired carbon fiber properties. Because of these differences, the cost of acrylic precursor fibers is three to five times greater than that of acrylic fibers used in textile applications.

Stabilization of PAN involves heating the fiber in air to temperatures ranging from 200° to 300°C for approximately 1 hour. The stabilization treatment is followed by carbonization in an inert atmosphere at temperatures greater than 1200°C. Orientation of the graphite-like crystal structure, and thus the fiber modulus, can be further increased by heat treatment (termed "graphitization") at temperatures up to 3000°C. The continuous carbon or graphite fiber is then surface treated and coated with a sizing agent prior to winding the continuous filaments on bobbins. The surface treatment is an oxidation of the fiber surface to promote adhesion to the matrix resin in the composite, and the size promotes handleability and wettability of the fiber with the matrix resin.

Carbon fiber strength is primarily controlled by the defect level, and modulus is controlled by crystalline orientation and degree of crystallinity. Thus, by varying those process parameters that can influence orientation and

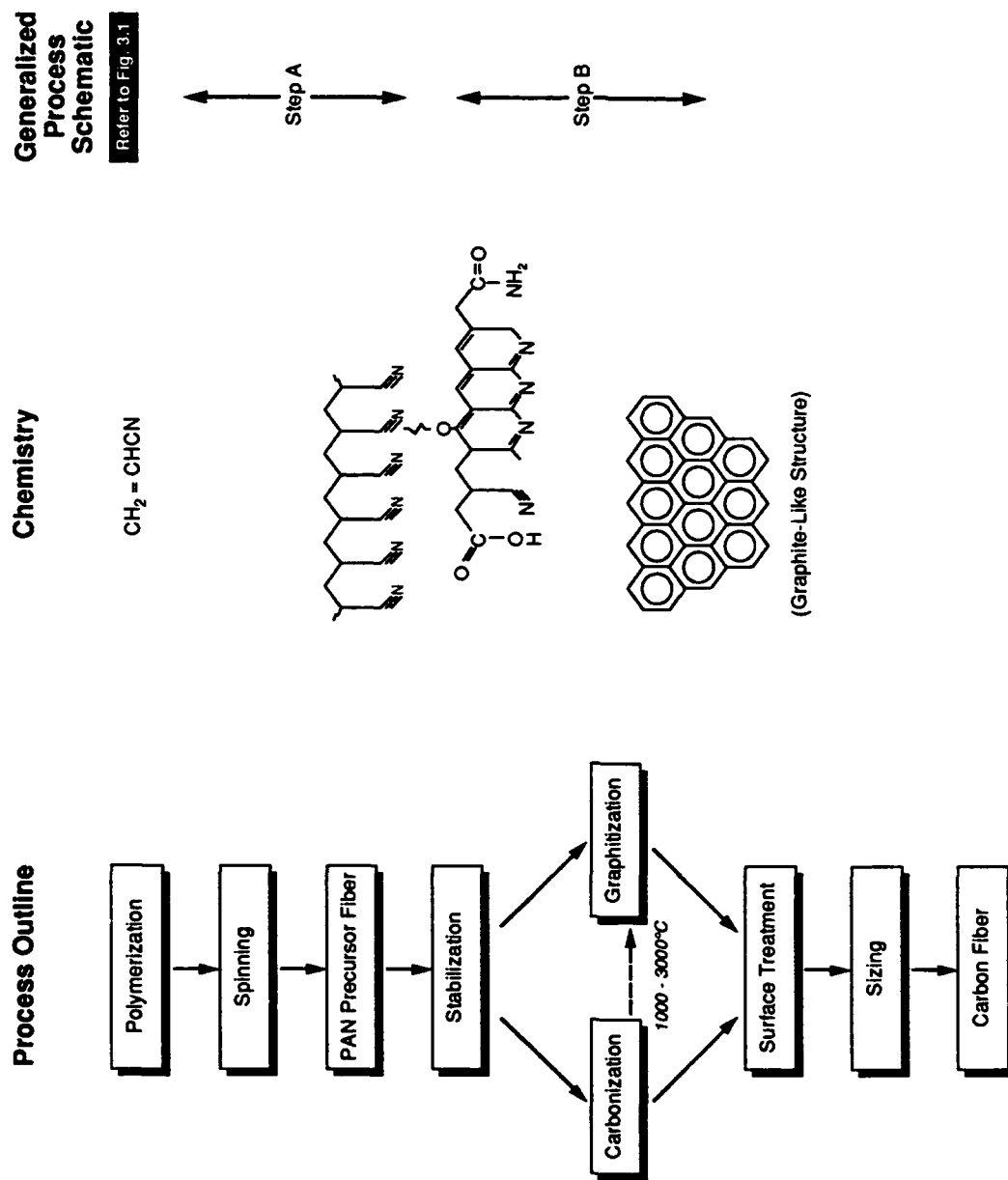


FIGURE 3.3 PAN Based Process

crystallinity (e.g., precursor purity, stretch ratios, overall process tension levels, carbonization furnace temperature,) in the manufacture of both the precursor and the carbon fiber, the resulting carbon fibers can have a broad range of properties. Generally, carbon fibers are classified into three major groupings (see Table 3.1): standard or aerospace grade, intermediate modulus (I.M.), and high modulus (H.M.). To date, most sales and aerospace qualifications have been with the standard-grade carbon fiber, and this is likely to continue as long as the present applications continue in production. The newer aerospace (and some recreation) applications, however, are primarily involved with the I.M. and H.M. fibers.

TABLE 3.1 Carbon Fiber Classifications

| Grade               | Product Modulus | % Strain to Failure | Development Activity  |
|---------------------|-----------------|---------------------|---|
| Standard            | 32-35           | 1.6                 | Lower Cost  |
|                     | 32-35           | 2.0                 | Increased Strain to Failure                                       |
| Intermediate (I.M.) | 40-50           | 2.0                 | Improved Composite Balance of Properties (Compression, Toughness) |
|                     |                 |                     | Increased Strain to Failure                                       |
| High Modulus (H.M.) | 55-85           | 1.0                 | Increased Strain to Failure                                       |

Carbon fibers possess the highest specific modulus (modulus/density) of all commercially available reinforcing fibers (several times that of conventional metals). However, since commercial PAN-based carbon fibers were first introduced 20 years ago, their physical properties have improved dramatically. In fact, over the past 7 to 8 years improvements in precursor as well as carbon fiber technology have increased the tensile strength of this class of fibers from approximately 3.45 GPa (500 Ksi) to 6.9 GPa (1000 Ksi). Today, specific strengths (tensile strength/density) achievable with PAN-based carbon fibers are among the highest of all commercially available reinforcing fibers. They also have a very good balance of properties, particularly compressive strength. Approaches toward improved compression performance, however, are an area where extensive research is being directed since polymeric-matrix composites (PMCs) made with the new higher-strength, higher-



modulus fibers show corresponding improvements in tensile and flex properties but little improvement in compression. A wide variety of fibers are now commercially available that range in tensile modulus from 207 GPa (30 Msi) to 586 GPa (85 Msi) with elongation from less than 1 percent to over 2 percent. Finally, a substantial amount of progress has been made in the ability to convert carbon fibers into intermediate product forms. The material can be braided, woven, knitted, and converted into unidirectional tapes that ultimately can be processed into composites. These materials, however, are inherently more difficult to handle than conventional textile fibers and conventional processing speeds are not practical with them. Very specialized techniques are therefore continually being developed to improve processing efficiencies.

Future Potential. Even though PAN-based carbon-fibers have been commercially available for over 20 years, the manufacturing technology, including both precursor and carbon fiber formation, is still very low on the technology growth curve, and there is great potential for improvements in product and process areas. Technological developments for PAN-based carbon fibers will center on the development and implementation of domestic precursor; lower-cost manufacturing technology (e.g., reduced capital as well as operating costs); new high-strength, intermediate, and high-modulus fibers; fibers with an improved overall balance of mechanical properties (e.g., compression); improved composite performance through optimization of the fiber and matrix interface; tailored physical properties (i.e., independent control of electrical and mechanical properties); and improved thermal oxidative stability.

Precursor Technology. Currently, all commercial production of PAN-based precursor fibers is based on solution spinning of PAN polymer. Typically, a dilute solution of acrylic polymer is extruded into a coagulation bath (wet spinning) or a hot-gas environment (dry spinning). The use of large amounts of solvents is a fundamental factor in the production process, which results in environmental as well as product design limitations. As indicated previously, all of the major U.S. carbon fiber producers have installed or will be installing domestic precursor capacity principally to meet the Department of Defense's precursor directive. Most of these companies are simply installing the standard wet or dry spinning technology that is the domestic equivalent of the technology used overseas to produce their precursor. However, one company, BASF Structural Materials, Inc., has developed and is now commercializing a unique new technology that utilizes melt-assisted extrusion as the basis for the spinning process.<sup>3</sup> This process eliminates the need for conventional solvent-recovery systems, reducing the required wastewater treatment. In short, this new process can easily produce the current standard high-quality precursor fiber, but it also has the versatility to modify fiber composition and even fiber cross-sectional shape, offering the potential to create a new family of carbon fibers with unique properties.

Carbon Fiber Technology. The development of processes capable of yielding higher-strength, higher-modulus, PAN-based carbon fibers is a critical research goal. Most of this research is centered around routes to eliminate defects from the fiber (the strength is flaw controlled), to obtain

higher orientation during processing, and to obtain a more uniform radial structure. Another major research initiative is in improving the carbon fiber surface chemistry in order to optimize the interface between the fiber and the resin, the weak link in the composite. Fiber surface chemistry can be modified via a number of methods, including overall process modifications, improved fiber coatings, enhanced surface oxidation techniques, and grafting reactive species onto the fiber surface.

Increased composite compression performance from the newer higher-strength, higher-modulus fibers is another goal that may be realized through additional process developments. The key to this problem is having a fundamental knowledge of the compression failure mode(s) and then altering the carbon fiber process/product to avoid premature failure. Some of the approaches being evaluated include modified precursor morphology, improved surface treatment techniques, and use of noncircular-shaped carbon fibers (available via the melt-assisted precursor technology).

The second major thrust of carbon fiber process research (after higher-performance fibers) is lower-cost fibers. The primary factors controlling the current cost of PAN-based carbon fibers are the low carbon fiber yields (approximately 50 percent) inherent in the use of acrylic polymers, acrylic precursor cost, and the high capital intensity and low productivity of the process. The first factor represents one of the single most important components in reducing costs; however, there is very little that can be done about it short of developing an alternate precursor polymer. Some work in this area has been done, particularly in Japan, but a new high carbon content, nonpitch, non-PAN polymer will be many years in development. Use of a lower-cost precursor (e.g., very high filament counts possibly approaching textile deniers) coupled with improved stabilization and carbonization processes are the key steps in the development of a lower-cost carbon fiber. Such a fiber would likely have substantially reduced mechanical properties, but they may be quite acceptable for some industrial and civil engineering applications. Both stabilization and carbonization are very energy intensive with low productivity. Development of an improved heat transfer process where stabilization can occur in seconds or minutes rather than hours is the key to next-generation stabilization. Such processes have been demonstrated in the laboratory, but none have yet been commercialized on a large scale.

As a result of the above efforts, it is projected that commercial carbon fibers with tensile strength well in excess of 6.9 GPa (1000 Ksi) and 2 percent elongation will be readily available. A common rule of thumb is that the theoretical strength should be about 10 percent of the modulus of a single crystal (approximately 1034 GPa in the case of graphite). Thus, carbon fiber in its current strength level range is about 15 to 20 times below the theoretical strength limit. Ultimately, how high the strength will rise is an open question, depending, as previously indicated, on the effectiveness of approaches to eliminate fracture-initiating sites. Efforts will continue toward the development of higher strain-to-failure fibers at all modulus levels. Improvements will also be made in fiber/resin systems such that composites with compressive strengths in excess of 2.8 GPa (400 Ksi) will probably be obtainable. Continual improvements in manufacturing technology for high-to-medium performance fibers will be coupled with substantially

larger carbon fiber capacities to yield declining pricing (constant dollars). Development of a lower-cost, lower-performance fiber (\$8-\$10/lb) with significant cost savings over conventional fibers is possible in the 1990s using a PAN-based precursor; a truly low-cost fiber would probably require a non-PAN precursor and is not likely before the turn of the century. Finally, all major U.S. carbon fiber suppliers will install domestic precursor capacity. This massive undertaking will require a significant technical effort and expense directed toward product requalifications and new product introductions. A positive outgrowth of this effort will be a natural evolution of the overall carbon fiber technology toward fulfilling specific U.S. market needs.

### *Pitch-based Carbon Fibers*

Technical Description and Present Status. The production of high-modulus, pitch-based carbon fibers begins by heat treating a petroleum or coal tar pitch feedstock to produce a liquid crystal precursor, termed "mesophase." The liquid crystal material is melt spun into a precursor fiber that is converted into a carbon fiber in a process somewhat analogous to that used for PAN-based carbon fiber. The high degree of molecular orientation of the as-spun fiber allows it, unlike PAN, to develop a truly graphitic crystalline structure during the carbonization/graphitization step. The fundamentals of the process are well documented in the literature,<sup>4,5</sup> and an overall schematic of the process is shown in Figure 3.4.

Potential advantages for pitch-based carbon fibers include economics and unique properties that result from their high degree of molecular orientation. Since the starting carbon content for pitch precursor is significantly higher than PAN precursor (approximately 93 percent versus 68 percent), the theoretical yield for pitch fibers is very substantially higher than that of PAN fibers. Also, acrylonitrile, which is the raw material for PAN-based carbon fibers, costs almost twice as much as the raw pitch used to produce pitch-based carbon fibers. These differences should make pitch-based fibers much less expensive than PAN-based carbon fibers. However, today's selling prices for these two varieties of carbon fibers are nearly identical. The likely cause for this is the limited manufacturing experience in pitch-based fibers. However, in the future it is probable that at least some portion of this potential cost advantage will be realized.

Pitch-based carbon fibers exhibit the highest specific modulus (tensile modulus/density) among the commercially available reinforcing fibers. Presently, pitch-based carbon fibers are available with moduli as high as 965 GPa (140 Msi). Their graphite structure also allows pitch-based fibers to possess excellent axial conductivities (both electrical and thermal) and very low axial coefficient of thermal expansion. Commercial pitch-based fibers are available with thermal conductivities that are three to four times that of copper. Because of this, pitch-based carbon fibers are preferred for space applications where stiffness, thermal expansion, or conductivity are critical. However, the extended graphite structure of present commercial pitch-based fibers also makes them more sensitive to fiber surface defects and structural flaws. This increased sensitivity causes the tensile strength of these fibers to be 40 to 50 percent lower than that of PAN-based carbon fibers. Also, it

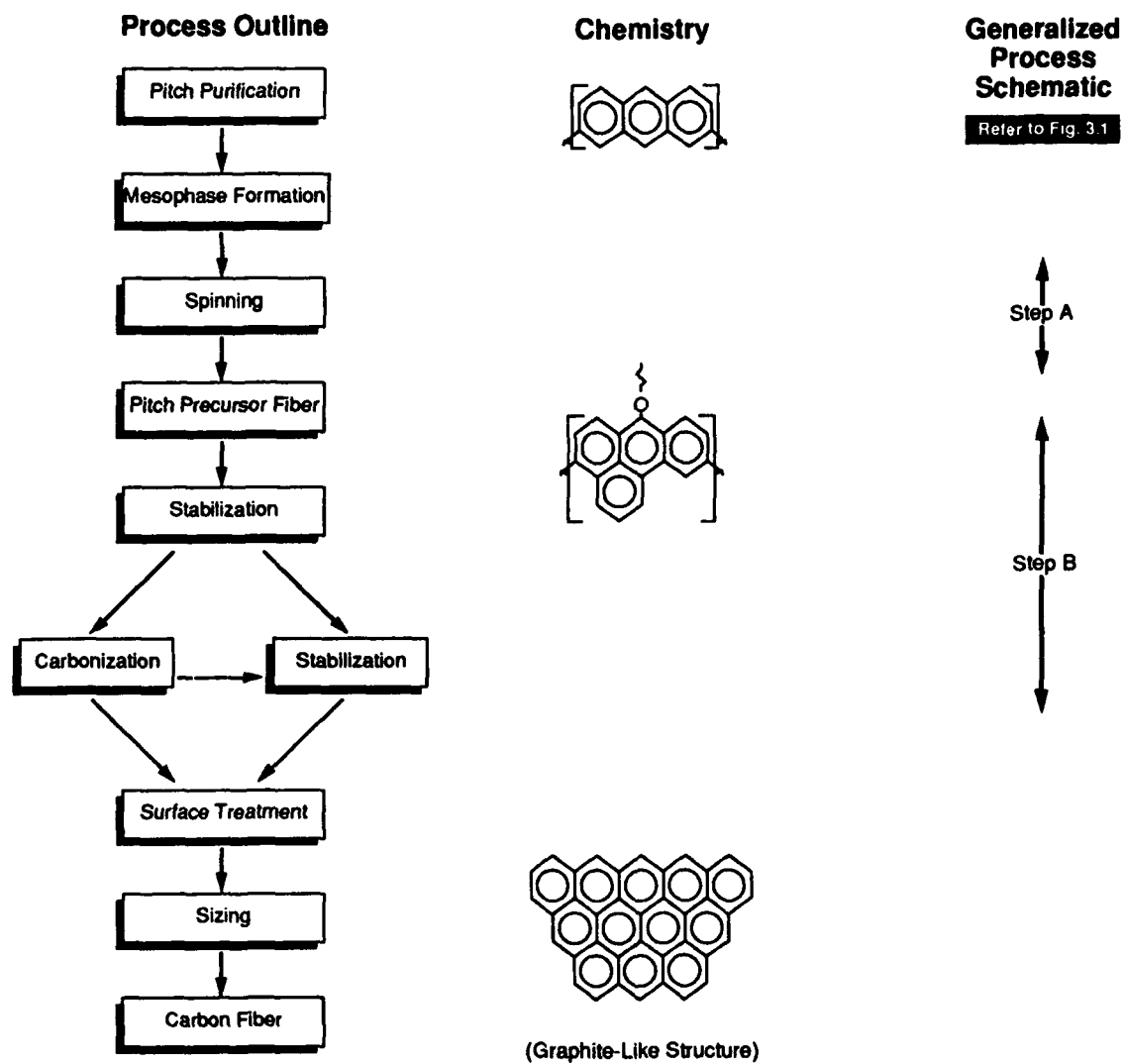


FIGURE 3.4 Pitch Based Process

results in a compressive strength for pitch-based carbon fibers that is only one-third that of PAN-based fibers.

Future Potential. In the area of pitch-based carbon fibers, the technical programs will be directed toward higher tensile strength products, fibers with improved compressive properties, improved routes to mesophase production, fibers with improved conductivity, and fibers that have improved processability. As indicated earlier, there is a substantial amount of interest in pitch-based fibers for their excellent conductivity, which offers opportunities in military, industrial electronic, and structural applications. Research in this area will continue, and fibers with even higher thermal conductivities will most certainly be developed. It should be noted that only pitch-based carbon fibers (and vapor-grown carbon fibers) have the graphite crystal structure needed to develop high thermal conductivity; this property creates a unique market for this fiber. Improved mesophase production techniques are a key to both improved process economics as well as improved products. The other key is reducing the flaw sensitivity of the fiber. Recent research shows that by modifying the microstructure of the pitch-based fiber during the spinning process, without significantly altering the crystalline orientation, it is possible to improve both the fiber tensile strength (reduced flaw sensitivity) and the compression strength.<sup>6</sup> In just the past 2 years pitch-based fibers with new microstructures have been introduced that have tensile strengths as high as 3.9 GPa (570 Ksi), compared with 2.4 GPa (350 Ksi) for the best previously available pitch-based fibers. In the future it is anticipated that fibers with tensile strengths in excess of 7.0 GPa (1000 Ksi) will be produced commercially and that compressive strength can be increased significantly over present values. Even though commercial pitch-based fibers have reached 93 percent of the modulus of perfect graphite, their tensile strength is less than 4 percent of that predicted by theory. Obviously, considerable improvement in the tensile strength of pitch-based carbon fibers is possible. Currently, as in the case of PAN-based carbon fibers, noncircular pitch-based carbon fibers are being evaluated as a route to higher-performance fibers that yield composites with improved properties.<sup>6,7</sup>

As mentioned previously, a key component in the development of a low-cost pitch product is improving the economics of the mesophase preparation step. Currently, the purification, preparation, and spinning operations are very expensive. If, in the future, a lower-performance, high-filament-count, pitch-based carbon fiber can be made for \$11 or less per kilogram, industrial, automotive, and civil engineering applications would create a substantial market for this variety of carbon fiber. The Japanese have been very active in the development of advanced pitch technology and could have the lead in the development of such a process/product.

#### *Other Precursors for Carbon Fibers*

Today, PAN and pitch are the principal precursors used to produce commercial carbon fibers. Even though the carbon content of PAN is 68 percent, the actual carbon yield after carbonization is only about 54 percent. This means that 46 percent of the mass of the precursor fiber is lost during its conversion to carbon fiber. Pitch contains over 90 percent carbon, but

the isotropic pitch must be converted to a mesophase if a high-performance fiber is to be produced. During this conversion process a significant fraction of the starting pitch is often lost. Obviously, research continues on other precursors for carbon fibers.

In the 1960s, Japanese researchers began studying polyvinylchloride (PVC) as a possible precursor. Unfortunately, the physical properties of the fibers produced from PVC precursor have been disappointing, and the net conversion of PVC to fiber has been less than 30 percent. However, it is possible that other precursors, or precursor preparation processes may be developed which significantly increase conversion. Polymers such as polyphenylene have a carbon content of 96 percent. If high molecular weight polymers such as polyphenylene can be produced commercially, they may replace PAN and possibly pitch as carbon fiber precursors and significantly alter the process economics.

Supercritical extraction is typical of pitch-separation techniques which could significantly change the economics of pitch-based carbon fiber processes. Such techniques could permit the preparation of a mesophase precursor with the regular molecular character of a synthetic polymer. This could not only increase conversion but also greatly ease the melt spinning process, reducing the cost of pitch-based carbon fibers.

#### Observations and Conclusions

- Carbon fibers, as a class, are known for their specific strength and modulus properties.
- Carbon fiber is likely to be the dominant high-performance reinforcing fiber in future ambient structural applications.
- Carbon fiber will probably be the first high-volume, high-performance fiber produced at a relatively low price.
- Even though both pitch and PAN-based carbon fibers are commercially produced, they are not mature products. Thus, it is likely that in the future their cost will decrease and their physical properties will significantly increase. A critical ingredient in these developments will be improved precursor technology.
- Considerable improvement is needed in the balance of properties possessed by both pitch and PAN-based carbon fibers (particularly compression strength). This will be vital if carbon fibers are to make further penetration in military applications (primary structures).
- In the near future, pitch fibers will likely dominate applications requiring high modulus and high thermal conductivity and, perhaps, increased resistance to oxidation. On the other hand, the small crystallite size typical of PAN-based carbon fibers will probably lead them to dominate in intermediate-modulus, high-strength applications.

- Pitch-based carbon fibers have the long-range potential to yield a substantially lower cost process than PAN-based fibers due to higher theoretical yields and lower carbonization costs. However, the approaches to reduced manufacturing costs for both fibers have some common features: improved precursor operating/capital costs, improved heat transfer processing operations for the conversion of precursor to carbon fiber, and use of larger precursor tows.

- The family of pitch and PAN-based carbon fibers encompasses a broad range of thermal and electrical conductivity. This set of conductivity properties is useful for a number of applications in which electromagnetic properties are at least as important as the mechanical properties of the reinforcing fiber. Currently, the mechanical and electromagnetic properties cannot be independently modified. Further research should be conducted in this area in order to be able to produce carbon fibers with tailored mechanical and electromagnetic properties.

## SILICON CARBIDE AND SILICON NITRIDE FIBERS

### Introduction

The ability to transform silicon-based organometallic polymers to silicon-based ceramic fibers was recognized in the mid-1970s.<sup>8</sup> About the same time the desirability of a high-modulus, high-strength, thermo-oxidatively stable, low-conductivity fiber for a variety of aerospace, defense, and consumer applications became apparent. For structural applications above about 1100°C, carbon-fiber-based composites (without special protective treatment) fail due to poor oxidation stability; most bulk ceramics, including the common oxide ceramics, fail due to poor mechanical stability. Nonoxide ceramics (e.g., silicon carbide [SiC] and silicon nitride [Si<sub>3</sub>N<sub>4</sub>]), are attractive candidates but suffer from low toughness and susceptibility to thermal shock. A method of overcoming these deficiencies is to reinforce the bulk ceramic of choice with thermally and oxidatively stable ceramic fibers. While many matrix systems are available, the technology for converting ceramics to fibers exists only for a small number of systems. Preparation of plastic-matrix fiber-reinforced composites with mechanical properties like those produced by carbon fiber, but with lower electrical conductivity, is also of interest. These considerations have led to a focus on the production of continuous SiC and Si<sub>3</sub>N<sub>4</sub> fibers over the past decade. Several of these products are now commercially available through Japanese suppliers, such as Nippon Carbon Company and Ube.

### Technical Description

To a first approximation, the technology for the production of Si ceramics from polymeric precursors is analogous to the general process shown in Figure 3.1. As shown in Figure 3.5, after polymerization the polymer is melt spun (other possible fiber-forming processes have not been systematically investigated). Next the resulting fiber is cured through a thermochemical cross-linking step ("preoxidation"), and the stabilized fiber is then fired to

form the desired ceramic. Three basic differences from carbon fiber processing, however, dominate the Si ceramic fiber technology. They are:

- The insensitivity of final fiber properties to orientation steps during processing
- Detrimental effects of oxidative crosslinking on ceramic fiber properties. In carbon fiber production, oxygen containing moieties less thermodynamically stable than the desired carbon structure are expelled from the structure during pyrolysis. In Si-based ceramics  $\text{SiO}_2$  is the thermodynamically most stable form and the compound least desirable in the final ceramic structure.
- Carbon fiber is normally produced from high molecular weight, mechanically sound, environmentally stable precursor fibers amenable to fiber-handling technology. The precursors for silicon-based nonoxide ceramic fibers are brittle and environmentally unstable, leading to major difficulties in handling and storage. This results in fibers of relatively short lengths and a high degree of variability.

Over the past few years it has been shown that the strength of  $\text{SiC}$  and  $\text{Si}_3\text{N}_4$  fibers is a very strong function of the flaw content of the final ceramic and that this flaw content is, to a very large extent, a function of impurities and lack of homogeneity in the starting polymer. It was further shown that strength loss at elevated temperatures and in various chemical environments is, to a significant degree, caused by exacerbation of existing flaws rather than by creation of new ones. It was also established that all Si-based ceramic fibers derived from polymeric precursors are classically brittle materials and that they all fit a universal curve of strength (at room or elevated temperature) versus reciprocal root of flaw size, as shown in Figure 3.6.

While linear, high molecular weight, Si-containing polymers of excellent spinability are known, these are not useful as precursors for ceramic fibers because, under the condition needed to cure the fibers, thermodynamically stable Si ring systems are formed and fiber integrity is lost. To overcome the ring-formation tendency, precursor polymers of low molecular weight and high degree of branching are used. Some of the more commonly used precursor structures are shown in Figure 3.5. All of these polymers contain non-stoichiometric amounts of Si, C, nitrogen, and oxygen (based on the desired final ceramic), and are difficult to characterize. All of these factors make continuous spinning of infinite-length fibers and yarns both difficult and expensive.

As already stated, to maximize ceramic fiber properties, the cure step must minimize introduction of oxygen and, because of fiber instability and brittleness, be kinetically compatible with spinning speeds as much as possible.



## Precursor Chemistry

| Chemical Structure  | Source                                 | Ceramic Fiber |
|---|--|---------------|
| • Polycarbosilane<br>$\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{Si}}}\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{Si}}}\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{--}$  | Nippon Carbon                          | Nicalon       |
| • Methylpolydisilylazane<br>$\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{Si}}}\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{Si}}}\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{N}}}\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{Si}}}\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{Si}}}\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{N}}}\text{--}$ | Dow Corning/Celanese<br>(experimental) | MPDZ          |
| • Hydridopolysilazane<br>$\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{Si}}}\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{N}}}\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{Si}}}\text{--}\overset{\text{H}}{\underset{\text{H}}{\text{N}}}\text{--}$  | Dow Corning/Celanese<br>(experimental) | HPZ           |
| • All polymers are: <ul style="list-style-type: none"> <li>– Highly branched (C containing)</li> <li>– Low molecular weight</li> <li>– Low aspect ratio</li> <li>– Difficult to characterize</li> </ul>   |  |               |

## Fibers from Preceramic Polymers

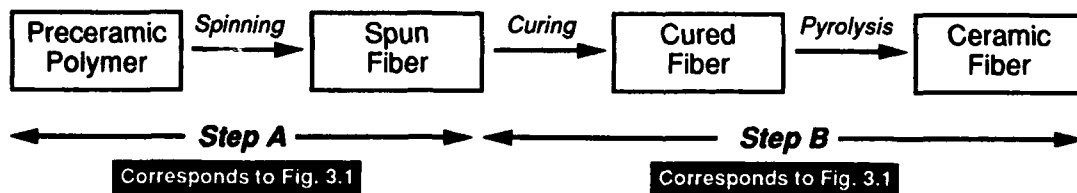


FIGURE 3.5 Production of Si Ceramic Fibers from Polymeric Precursors.

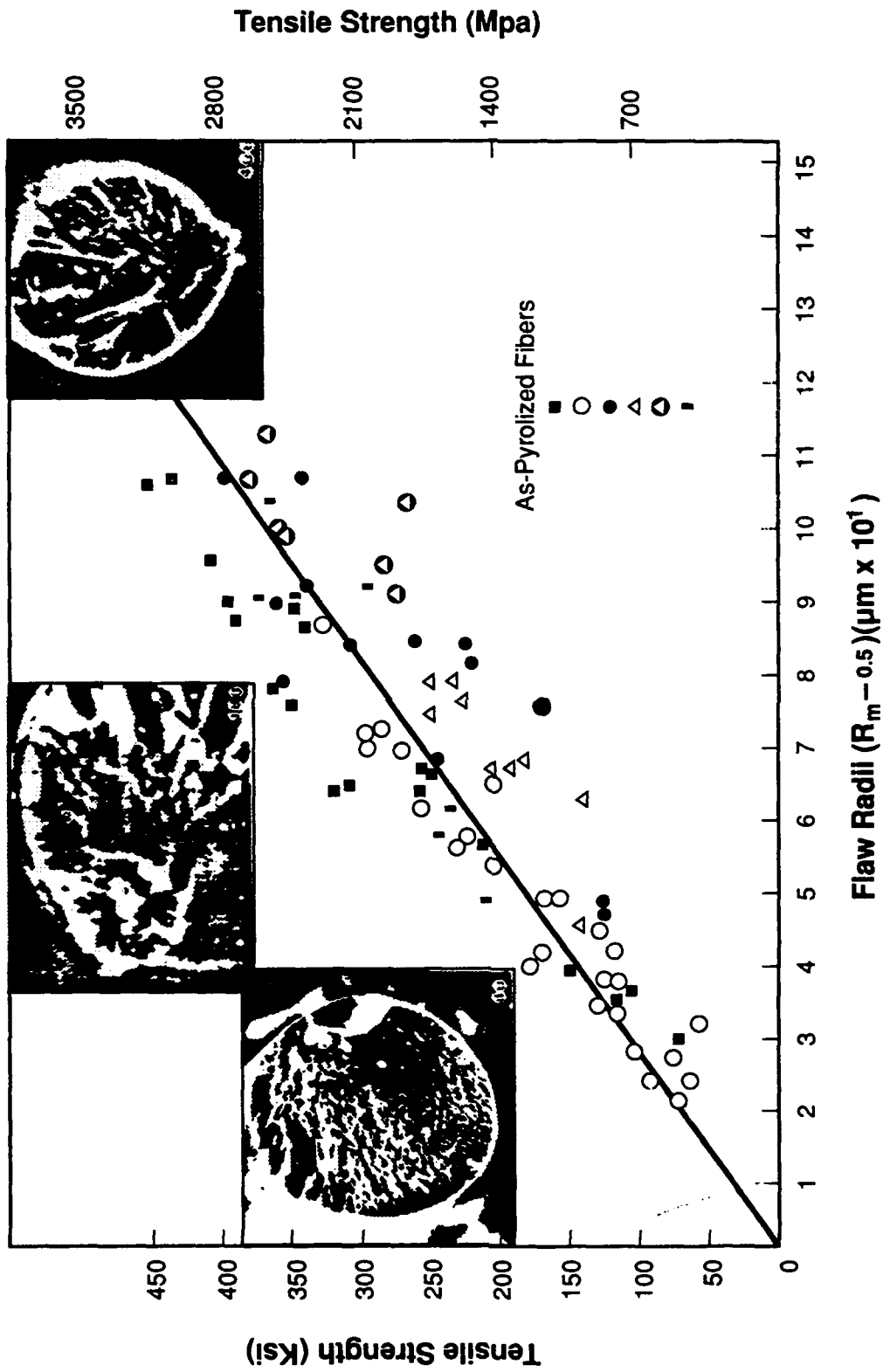


FIGURE 3.6 Variation of tensile strength with flaw size.

An advantage of the HPZ system developed by the Defense Advanced Research Projects Agency/Air Force Materials Laboratory (Dow Corning, Celanese) is the ability to chemically cure the precursor fiber at high speeds.

Pyrolysis of cured fiber to form the ceramic is straightforward, with final properties dependent on time, temperature, and chemical environment. Typically, fibers are obtained with moduli in the range of 25 to 30 Msi, strengths in the range of 300 ksi, and densities of about 2.5 g/cm<sup>3</sup>. While useful, the modulus of these fibers is considerably less than that of the dense ceramic, and the chemical and thermal behavior of the fibers is also reduced from that typical of SiC or Si<sub>3</sub>N<sub>4</sub>. Chemically, no Si ceramic produced from a polymeric precursor is stoichiometrically correct, and these materials are better described as SiC-like or Si<sub>3</sub>N<sub>4</sub>-like. Physically it has been shown that in all cases the structure of the fiber is essentially amorphous or consists of very small SiC or Si<sub>3</sub>N<sub>4</sub> crystals sitting in an amorphous matrix. This similarity of physical structure is the rationale for the observed "universal" strength response and low modulus of these fibers. The porosity of these structures is difficult to characterize, but it probably plays a role in the low level of observed properties.

#### Technical Future

The production of SiC-like or Si<sub>3</sub>N<sub>4</sub> fibers from polymeric precursors is well established and reasonably well understood. Technical directions that could lead to significant property improvements are identifiable and include:

- Improved stability and higher molecular weight precursor polymers.
- Polymers with reduced flaw concentrations as spun, in conjunction with improved process control throughout.
- Approaches to stoichiometrically correct ceramic chemistry to improve chemical stability.
- Approaches to ceramics with larger crystal size to create structures of improved physical stability.
- Densification of existing structures to remove residual porosity.
- Development of effective diffusion boundary coatings for ceramic fibers to block reactive gases from entering the fiber structure and exacerbating the existing flaw populations.

The present limitation to increased use of Si-based ceramic fibers is their very high cost. Unless it can be shown that improved properties will increase market acceptability at current prices, it is unlikely that major improvements in fiber technology will occur without major government support. Lower-cost fiber is a function of both raw material availability and process complexity. Improvements in these regards, while possible, are unlikely to be achieved without external pressures being brought to bear on potential

manufacturers. To date, no new or growing market capable of catalyzing the necessary research has been identified.

### Observations and Conclusions

The production of Si-based ceramic fibers from polymeric precursor is a demonstrated technology, and R&D programs can be identified that are highly likely to improve both fiber properties and fiber cost. Although the organometallic polymer approach to ceramic fibers could be extended to other ceramic systems, these R&D programs are expensive and time consuming and must involve, in addition to the identification of new materials and processes, the scale-up of proposed improvements to show that feasibility can be transformed into commercial reality.

## OXIDE FIBERS

### Introduction

Ceramic oxide fibers can be prepared by any of the processes identified as polymeric, polymer-modified solutions or dispersions, fiber-forming salt solutions, or sol-gel systems, the latter sometimes being used as an all-inclusive term for all of these when applied to the preparation of nonvitreous ceramic fibers by pyrolytic conversion processes.<sup>9</sup> Most of these fibers have been fabricated by processes that can be categorized generally under "pyrolytic conversion of precursor fibers." Although the information usually provided may disclose the general type of processing by which these fibers are prepared, for example, polymeric or sol-gel (sol is a colloidal dispersion in a liquid medium), details are generally not sufficient for their immediate duplication. The most extensive amount of published information on ceramic fiber processing is in patents, the reference of Bracke et al.<sup>2</sup> having been cited in Chapter I. A number of publications over the past several years have provided data on properties of ceramic oxide fibers currently available either commercially or on an experimental basis.<sup>1,9,10</sup>

Oxide fibers prepared from the precursor pyrolysis process and that are currently available or under development are listed in Table 3.2. These fibers are, in principle, desirable for high-temperature applications where the potential for oxidation exists. Except for the NEXTEL Z-11 ceramic fiber of 3M, all of the oxide fibers in the table contain a major  $\text{Al}_2\text{O}_3$  component. The  $\text{ZrO}_2$ - $\text{SiO}_2$  fiber is not generally claimed to be of reinforcement grade since its modulus of elasticity is relatively low (76-90 GPa) (11-13 Msi).<sup>11</sup> However, fabric made from this fiber does have outstanding resistance to flame penetration, and it may be useful for applications requiring such properties.

### Polymeric Precursors

Preparation of oxide fibers from polymeric precursors is closely related to the processing of carbon or graphite fibers. However, polymerization of precursors for oxide fibers usually involves hydrolysis of the precursor. Wainer et al.<sup>12</sup> (Horizons, Inc.) prepared polymer precursors for the oxides of

TABLE 3.2 Oxide Fibers

| Identity                                 | Composition<br>(wt. %)   | Approximate<br>Diameter<br>( $\mu\text{m}$ ) | Manufacturer                          |
|--|--|--|---------------------------------------|
| Fibre                                    | $\text{Al}_2\text{O}_3$ (100)  | 20   | E.I. duPont de Nemours<br>& Co., Inc. |
| PRD-166 <sup>a</sup>                     | $\text{Al}_2\text{O}_3$ (80)<br>$\text{ZrO}_2$ (20)                                    | 20   |                                       |
| Saffil <sup>b</sup>                      | $\text{Al}_2\text{O}_3$ (96)<br>$\text{SiO}_2$   | 3  | Imperial Chemical                     |
| Safimax <sup>c</sup>                     | $\text{Al}_2\text{O}_3$ (96)<br>$\text{SiO}_2$ (4)                                     | 3  | Industries, plc, Ltd. (ICI)           |
| Sumica <sup>a</sup>                      | $\text{Al}_2\text{O}_3$ (85)<br>$\text{SiO}_2$ (15)                                    | 17   | Sumitomo Chemical Co., Ltd.           |
| Alcen <sup>b</sup>                       | $\text{Al}_2\text{O}_3$ (80)<br>$\text{SiO}_2$ (20)                                    | 2-3  |                                       |
| Denka continuous<br>alumina fiber        | $\text{Al}_2\text{O}_3$ (80)<br>$\text{SiO}_2$ (20)                                    | 10   | Denka KK                              |
| Alumina<br>continuous fiber <sup>a</sup> | $\text{Al}_2\text{O}_3$ (99.5)   | 10-12  | Mitsui Mining Co., Ltd.               |
| Nextel 312 <sup>a</sup>                  | $3\text{Al}_2\text{O}_3/1\text{B}_2\text{O}_3/25\text{SiO}_2$<br>(molecular ratios)    | 10-12  | 3M Co.                                |
| Nextel 440 <sup>a</sup>                  | $3\text{Al}_2\text{O}_3 2\text{SiO}_2$ (98)<br>$\text{B}_2\text{O}_3$ (2)              | 10-12  | 3M Co.                                |
| Nextel 480 <sup>a</sup>                  | $3\text{Al}_2\text{O}_3 2\text{SiO}_2$ (98)<br>(mullite)<br>$\text{B}_2\text{O}_3$ (2) | 10-12  | 3M Co.                                |
| Nextel Z-11 <sup>a</sup>                 | $1\text{ZrO}_2/1\text{SiO}_2$  | 11   | 3M Co.                                |

<sup>a</sup> Continuous filament form.  
<sup>b</sup> Staple.  
<sup>c</sup> Semicontinuous  
<sup>d</sup> Partially stabilized.

aluminum, yttrium, and the lanthanides, the group IV-A metals (titanium, zirconium, hafnium, and thorium) and the metals having atomic numbers 23-28 inclusive. Polymers were prepared from aqueous solutions of concentrated carboxylate salts by heat treatment in a closed vessel at 60° to 90°C. The resulting polymers had oxide yields (after calcination and oxidation) of up to

90 percent (in the case of  $\text{ZrO}_2$ ). Preparation of continuous, 6- $\mu\text{m}$ -diameter monofilaments of  $\text{ZrO}_2$  by extrusion and drawing of the polymer followed by controlled firing to temperatures up to  $1250^\circ\text{C}$  was described. The products of this work were generally characterized as being transparent (or almost transparent), flexible, and microcrystalline. The polymeric precursor approach has been successfully applied by Horikiri et al.<sup>13</sup> in the preparation of alumina-silica fibers. This work is apparently the foundation for SUMICA, an alumina-silica fiber comprising 85 percent  $\text{Al}_2\text{O}_3$  plus 15 percent  $\text{SiO}_2$ , which is manufactured by Sumitomo Chemical Co., Ltd. The precursors for  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  fibers comprised a spinning solution of an organic solvent, such as benzene or dioxane, a polyaluminumoxane for  $\text{Al}_2\text{O}_3$  fibers, and a mixture of the polyaluminumoxane solution with a silicon-containing compound for  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  fibers. The solutions were spun into continuous filaments that were subjected to humid air for hydrolysis. Precursor fibers were then fired to temperatures between  $600^\circ$  and  $1700^\circ\text{C}$  for conversion to the oxide fibers.

#### *Spinnable Salt Solutions*

Oxide precursor fibers may be prepared by spinning solutions such as aqueous solutions of carboxylate salts (e.g., aluminum formoacetate).<sup>14,15</sup> At the present time, no commercial continuous filament products are believed to be manufactured by this approach.

#### *Polymer- and Solution-Modified Sols and Slurries*

At the present time, the majority of continuous filament products are based on precursors comprising sols or slurries modified by salt solutions and/or organic polymers. Polymers may be added solely to provide the rheological properties necessary for fiberizing, but the presence of this thermally decomposed (i.e., fugitive) component may also affect the nucleation processes of the inorganic phase and thus affect the properties of the resultant fiber and the microstructure.<sup>16-18</sup> The organic modifier may not only provide the necessary properties to permit spinning but also act as a precursor for an inorganic component of the fiber composition. For example, aqueous basic aluminum chloride<sup>19</sup> and zirconium acetate solutions<sup>20</sup> were blended with silica aquasols for the preparation of  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  and  $\text{ZrSiO}_4$  (zircon) fibers, respectively. In these cases the salt solutions provided fiber-forming properties and served as pyrolyzable precursors for metal oxide components in the final ceramic fibers. Continuous filaments of  $\text{Al}_2\text{O}_3$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  and  $\text{ZrO}_2$ - $\text{SiO}_2$  compositions with essentially unlimited length were also prepared in relatively early developments with this general approach.<sup>21,22</sup>

Continuous filament products of essentially pure  $\text{Al}_2\text{O}_3$ , or comprising a large percentage of  $\text{Al}_2\text{O}_3$ , have been reported as being prepared from modified slurries. Slurries differ from sols in that sols are generally considered as comprising colloidal particles predominantly less than  $0.10\ \mu\text{m}$  ( $100\ \text{nm}$ ) in size, while slurries comprise particles considerably larger. This difference in sizes of the suspended particles in sols and slurries is an important factor that affects many fiber properties, including optical transparency, smoothness, handleability, strength, microstructure, and performance at high temperatures. A modified slurry process is used to produce several commercially available fibers, including FP alumina ( $\text{Al}_2\text{O}_3$ ) and PRD 166 (80

percent  $\text{Al}_2\text{O}_3$  plus 20 percent partially stabilized  $\text{ZrO}_2$ ) from duPont and an alumina fiber from Mitsui Mining Company.

#### *Microstructure Development*

Pyrolysis of precursor fibers to form oxide fibers overlaps with the early stages of crystallization. After removal of fugitive components, sintering continues. Densification, removal of pores, compound formation, and grain growth all occur as in the sintering of other more traditional ceramic articles. Similarly, the microstructure that results is affected by the precursors that are used. The use of polymeric, solution, or sol-gel precursors as well as the low molecular weight of the inorganic components make it possible to control the earliest stages of crystallization. Thus, the fine microstructures which can be obtained are not achievable with more traditional powder processes. Resultant fibers with fine-grained polycrystalline microstructures may possess very high strength, excellent flexibility, and optical transparency. Microstructures attainable are illustrated in the electron micrographs of Figures 3.7 and 3.8 of NEXTEL 440 ceramic fibers that have been converted to mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ).<sup>11</sup> In this case, mullite grains are 20 to 60 nm in size. The development of microstructures in ceramic fibers prepared with sol-gel processes is discussed in more detail in other recent publications.<sup>1,23</sup> As might be expected, microstructures of oxide fibers prepared from fiberizable slurry-type dispersions will be considerably coarser. Fiber FP, and PRD 166, both manufactured by duPont, are characterized by  $\text{Al}_2\text{O}_3$  grains considered to be relatively large (e.g.,  $0.5\mu\text{m}$ , or 500 nm), as shown in the electron micrographs of Figures 3.9 and 3.10.<sup>19</sup>

The extreme differences in grain size of the NEXTEL mullite ceramic fibers and duPont FP alumina and PRD-166 alumina-zirconia fibers is obvious when one compares the micrographs of Figures 3.7 and 3.8 with those of Figures 3.9 and 3.10. The very fine microstructure of the NEXTEL ceramic fibers is largely responsible for its glass-like appearance and handling quality. Stacey<sup>10</sup> has suggested that very fine microstructures are related to high strength, but for high-temperature uses it is important to increase grain sizes because grain-boundary creep is expected to be slower with larger crystallites. Similarly, microstructural stability (i.e., minimizing changes in grain size) is an important requirement where strength and modulus must be retained.

Ceramic oxide fibers are, in principle, desirable for high-temperature applications where the potential for oxidation exists, and in this respect they are to be preferred over carbon or other nonoxide fibers. However, property data available on most ceramic oxide fibers has been obtained from testing at room temperature. Increasing amounts of data on tensile strength and modulus of elasticity are being obtained on fibers as they are being exposed to high-temperatures. Results have been reported in several recent publications.<sup>10,24,25</sup> Thermal expansion values, vitally important to successful utilization in composites for high temperature applications, are also available.<sup>26</sup> A review of these data shows that ceramic fibers begin to lose strength and modulus of elasticity at temperatures above  $800^\circ$  to  $1000^\circ\text{C}$ .

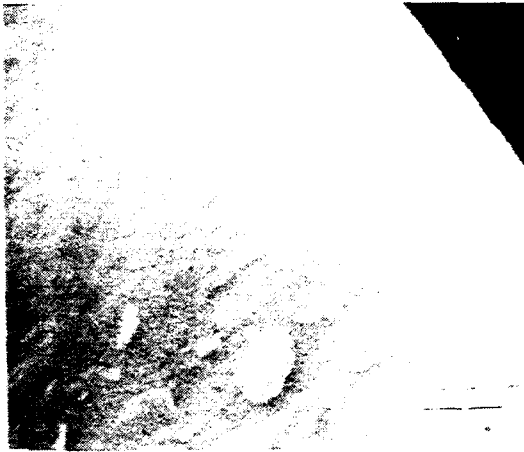


FIGURE 3.7. Scanning electron micrograph of fracture surface of mullite fiber (50 000x). Copyright © by the American Ceramic Society.



FIGURE 3.8. Transmission electron micrograph of ion milled section of mullite fiber (150 000x). Copyright © by the American Ceramic Society.

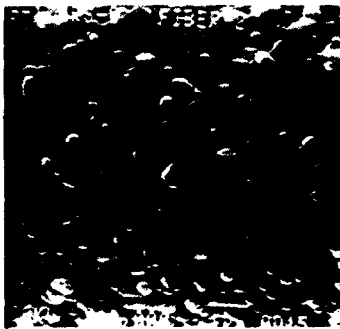


FIGURE 3.9. SEM of Fiber FP Surface Copyright © by the American Ceramic Society.

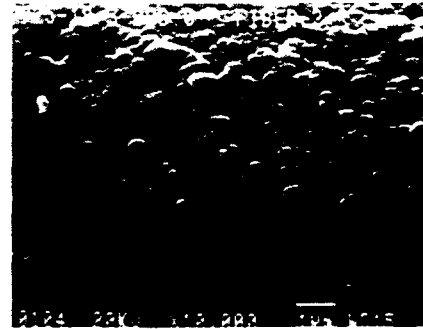


FIGURE 3.10. SEM of PRD-166 Surface Copyright © by the American Ceramic Society.



### *Technological Future for Oxide Fibers*

A review of the properties of the oxide ceramic fibers that are available at the present time discloses that they cannot meet many of the projected requirements for reinforcement of high-temperature composites requiring stable strength and stiffness properties and resistance to creep at high temperatures, (e.g.  $> 1200^{\circ}\text{C}$ ), for extended periods of time. New fibers of selected compositions will be necessary to satisfy these needs.

The controlled pyrolysis of precursor fibers has been shown to be a useful process for the fabrication of both oxide and nonoxide high-performance fibers for structural applications. It is a uniquely versatile process in that virtually any composition that can be compounded in a fiberizable precursor batch can be pyrolyzed to form continuous inorganic fibers. However, the preparation of fibers sufficiently handleable for use and possessing properties that would classify them as high-performance fibers requires sophisticated process control procedures tailored to each composition and adjusted for the precursor materials used. Survival of the filament form through pyrolysis does not necessarily guarantee a resultant high-quality fiber because it must undergo further heat treatment with associated solid-state reactions, crystal growth, and structural changes.

Fundamental studies on progressive microstructural changes that take place during the pyrolysis process as well as during sintering and densification of the resulting inorganic fiber would facilitate development of advanced high-performance inorganic fibers not now available. Especially important is the development of methods for stabilization of microstructures so as to prevent or minimize property changes during high-temperature applications.

## CHEMICAL CONVERSION OF A PRECURSOR FIBER

### Introduction

The chemical conversion of a precursor fiber (CCPF) is a versatile but not very well known fiber-making technology used by researchers from the early 1960s to the mid-1970s to develop a number of interesting refractory fibrous materials. As the name of the process implies, the method invokes the conversion of one fiber into another by reacting the precursor fiber with the proper reactants under precisely controlled conditions. Thus, the difficult task of forming the refractory fiber directly is bypassed. Instead, effort is focused on dealing with a chemical problem to accomplish conversion of an existing fiber into another.

The success of this method depends on two important factors:

- Selection of available fiber as precursor for the reaction.
- Control of reaction parameters to facilitate the reaction between the reactants and the precursor fiber.

In practice, commercially available fiber (e.g., carbon fiber) or fiber that can be easily produced (e.g., boric oxide fiber) is used as a precursor. It should be noted that once a product fiber is produced, it can itself be used as precursor fiber for other products. For example, BN fiber is made from  $B_2O_3$  fiber, and TiN fiber can be prepared by reacting BN fiber with a titanium chloride and hydrogen mixture.

The versatility of this fiber-making approach lies in the numerous combinations of gaseous reactants and precursor fibers that can be used. This is illustrated by the examples shown in Table 3.3.

TABLE 3.3 Refractory Fibers Prepared by Chemical Conversion of a Precursor Fiber

| <u>Fiber</u>   | <u>Melting Point (°C)</u> | <u>Precursor</u> | <u>Reactants</u>     |
|----------------|---------------------------|------------------|----------------------|
| BN             | 3000 (Sublimes)           | $B_2O_3$         | $NH_3F$              |
| TiN            | 2950                      | BN               | $TiCl_4 + H_2$       |
| NbN            | 2573                      | BN               | $NbCl_5 + H_2$       |
| $B_4C$         | 2450                      | C                | $BCl_3 + H_2$        |
| $Mo_2C$        | 2687                      | C                | $MoCl_5 + H_2$       |
| NbC            | 3900                      | C                | $NbCl_5 + H_2$       |
| $NbC_xN_{1-x}$ | —                         | C                | $NbCl_5 + H_2 + N_2$ |

Like any other processes, CCPF has its technical constraints, as follows:

- The desired fiber composition must be thermodynamically achievable from the precursor and reactants.
- The phase that forms initially in the conversion on the fiber surface must not be impervious to further diffusion of the gaseous reactants into the interior for continuous conversion.
- Since the conversion is accomplished by a diffusion-controlled process, the reaction rate may be slow, but the fine diameter of precursor fiber will favor the conversion kinetics.

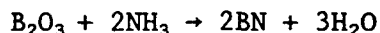
Among the examples listed in Table 3.3, two fibers, boron nitride and boron carbide, are of particular importance and interest.

#### Boron Nitride Fiber

Preparation of boron nitride (BN) fiber from boric oxide precursor was first reported by Economy et al. in 1966.<sup>27</sup> Subsequently, numerous articles were published that described the process, properties, and applications for this fiber.<sup>28-30</sup> From a process standpoint, the fiber was made by the following steps:

- Fiberization of  $B_2O_3$  melt to form  $B_2O_3$  fiber
- Nitriding of  $B_2O_3$  fiber with  $NH_3$
- Final stabilization to form BN fiber

Stoichiometrically, the conversion can be expressed in a simple chemical reaction:



The reaction mechanism, however, is actually quite complex. Microporous structure is developed from the initial reaction between boric oxide and ammonia. The formation of the microporosity permits diffusion of ammonia into the fiber core and escape of water from the interior through the reaction layer. This mechanism allows the conversion to proceed to completion.

In the early stage of development, BN fiber was produced in a staple roving form. The roving was then converted into various textile forms such as staple yarn, mat, fabric, braided structure, and felt. These product forms made thorough characterization of the fiber properties possible, as follows:

Mechanical properties:

|                         |                                |
|-------------------------|--------------------------------|
| Typical fiber diameter: | 4 to 6 microns                 |
| Tensile strength:       | 345 to 862 MPa (50 to 125 ksi) |
| Young's modulus:        | 27.6 to 68.9 GPa (4 to 10 msi) |
| Elongation at break:    | 2 to 3 percent                 |

Thermal stability: No significant weight loss at 2500°C in inert atmosphere.

Oxidation stability: Oxidation starts at ~850°C; further oxidation leads to formation of boric oxide coating on the fiber surface, which acts as a glaze and affords protection up to 1300°C.

Corrosion resistance: Excellent resistance against corrosive reagents as compared to carbon and glass fibers.

Electrical properties: Very low dielectric constant of 4.0 and low dissipation factor.

Thermal conductivity: High.

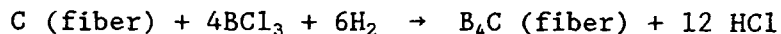
BN fiber is indeed a multipurpose fiber. Its many properties make it uniquely suitable for numerous potential applications, such as military clothing, radomes, insulation in particle accelerator coils, thermal insulation, electrical applications, filter bags, chemical filtration, high-energy battery separators, and printed circuit boards.

For BN fiber to be useful in the structural reinforcement area, its mechanical properties need improvement. In 1972 the method to produce high-strength, high-modulus BN continuous filament yarn was developed and

disclosed.<sup>31,32</sup> Improvements in mechanical properties were achieved by hot stretching the partially nitrided fibers. BN fiber with a tensile strength of 2070 MPa (300 ksi) and a modulus of 345 GPa (50 msi) was reported. In an unpublished work, test fibers exhibited a tensile strength of 3100 MPa (450 ksi) and a modulus of 480 GPa (70 msi). All these results showed the feasibility of producing BN fibers with superior mechanical properties suitable for structural applications. Further development work is required however, in order to produce high-modulus BN fibers in pilot quantity for application assessment purposes.

### Boron Carbide Fiber

Preparation of boron carbide ( $B_4C$ ) fiber was achieved by the reaction of commercially available carbon fiber with boron trichloride in the presence of hydrogen at  $\sim 800^\circ C$ .<sup>33-35</sup>



The formation of boron carbide depends on a diffusion-controlled reaction in which boron trichloride and hydrogen react with the precursor carbon fiber; a layer of boron deposit is formed first, and it subsequently reacts with carbon to form boron carbide. Further conversion depends on the diffusion of boron through the large interstitial openings of the boron carbide structure. Like other diffusion-controlled reactions, the conversion rate depends on the fiber diameter. Fine-diameter precursor fiber favors the conversion kinetics.

The diameter of the starting carbon fibers is about 8 microns. As the conversion proceeds, the fiber diameter increases according to the degree of conversion. The tensile strength and modulus of the product also increase, progressing with the enhancement of the degree of conversion. It is an advantage of this process that the properties of the product can be controlled by adjusting the degree of conversion during the reaction. The boron carbide fiber produced by this process often possesses crimps, which cause weakening of fiber properties. This shortcoming is eliminated by post reaction tensioning at an elevated temperature. At a temperature of  $\sim 2100^\circ C$  and a tensile stress of 20.7 to 27.6 MPa (3000 to 4000 psi), the boron carbide fibers are straightened, resulting in a drastic improvement in mechanical properties. Typically, boron carbide fibers display a modulus of 207 to 482 GPa (30 to 70 msi), and the tensile strengths for the straightened fiber are 2070 to 2760 MPa (300 to 400 ksi).

### Observations and Conclusions

The technology of CCPF is a versatile fiber-making method. There are several practical and significant aspects that are unique to this approach.

- The fiber-forming step is eliminated or greatly simplified, since commercially available fibers or fibers that can be readily produced are used as the precursors.

- CCPF is a chemistry-driven process that primarily involves gas-solid heterogeneous reactions. It is important to recognize that in CCPF the reaction is not limited to the surface. The conversion develops inward to the core of the fiber via a mechanism unique to each fiber.

- The fibers produced by CCPF are usually of fine diameter, which favors the kinetics of conversion.

- The composition of the product fiber is governed by the precursor fiber and the reactants used in the conversion, offering many new possibilities for exploration.

- Fiber properties can be further improved by post reaction treatment, such as crystallite orientation by hot stretching to improve modulus and strength in the case of BN and the removal fiber kinks also by hot stretching to improve strength in the case of  $B_4C$  fiber.

It must be pointed out that this technology is still in its early stage of development, the examples reported by early researchers having merely laid the groundwork for the technology. Efforts along the following lines may be fruitful:

- Experimental work on various combinations of precursor fibers with a variety of reactants directed at making fibers of interest. The effort will help to define the practical limits of the approach.

- Characterization and application development for the fibers made by this technology. Based on the results of application assessment, scale-up work should be done for selected fibers to provide a realistic basis for assessing costs.

## CHEMICAL VAPOR DEPOSITION

### Introduction

Chemical vapor deposition (CVD) fibers are formed by the deposition on a monofilament substrate of a species generated by a vapor-phase reaction occurring adjacent to or at the substrate surface. In general, the CVD reaction is initiated as a result of the substrate being heated, usually to incandescence. For production fibers the substrate continuously moves through the reaction apparatus or reactor, thus increasing in diameter through the processing, with the CVD fiber product being spooled or taken up downstream of the reaction chamber.

The formation of continuous fibers by the application of CVD technology has proven to be a reliable and routine approach to the production of consistent products such as boron and silicon carbide fibers. CVD processing has a wide range of applicability and flexibility in terms of chemical composition, and is limited only by the availability of volatile reactant molecules that incorporate the species to the deposited.

Two CVD fibers are now in production in the United States at TEXTRON Specialty Materials in Lowell, Massachusetts: boron on a tungsten substrate and silicon carbide using a carbon monofilament substrate. Silicon carbide fiber on a tungsten substrate is produced in the United Kingdom by British Petroleum. Substantial production facilities for both boron and silicon carbide fibers exist in the USSR.

New CVD fibers known to be currently under development include  $TiB_2$  and  $TiC$  on several substrates at TEXTRON Specialty Materials and at Amercom. Coatings involving  $TiB_2$  and  $TiC$  composites on silicon carbide fiber also are being investigated at these companies. Refractory Composites, Inc., is developing a process for depositing  $TiB_2$  on titanium wires by a plasma CVD process. Similarly, Professor Vladimir Hlavacek, of the State University of New York at Buffalo, is developing CVD fabrication methods for coating carbon and tungsten fibers with  $TiB_2$ ,  $TiC$ , and boron. A method for making potentially low cost carbon fibers via carbon CVD onto a carbon substrate grown in-situ also is under development. This process is being pursued mainly in two countries—in the United States by General Motors Research Laboratory and Hyperion International and in Japan by several companies and universities.

#### Technical Description

In view of their established position as actively used CVD fibers, it is instructive to provide some details on boron and the "SCS" series of silicon carbide fibers. Both fibers are continuous fibers produced by CVD on substrate wires that are pulled through glass reactor tubes. Boron fiber is currently produced in quantities of approximately 35,000 lb/yr, while silicon carbide ( $SiC$ ) monofilament production is less than 2000 lb/yr in the United States.

#### Boron Fibers

Boron fiber is a continuous monofilament produced in two nominal diameters, 4 mil (100  $\mu m$ ) and 5.6 mil (140  $\mu m$ ). Properties of the fiber, listed in Table 3.4, are compared with typical properties of other fibers, including silicon carbide. Almost all of the boron fiber produced is used to form a boron-fiber epoxy-preimpregnated tape ("prepreg"), a product form in which a linear parallel array of fibers is coated with an epoxy resin and backed on one side with a light fiberglass fabric. The tacky prepreg is then sold to users for ply lay-ups and part fabrication.

Figure 3.11 illustrates the boron fabrication process. A tungsten substrate wire, about 0.5 mil in diameter, is continuously drawn through a vertical glass reactor. Both ends of the reactor tube are sealed by a shallow pool of mercury, which acts as an electrical contact to the fiber. Electric power is applied across the ends of the reactor tube such that the tungsten becomes incandescent. A mixture of boron trichloride ( $BCl_3$ ) vapors and hydrogen ( $H_2$ ) gas is admitted to the reactor tube, and the reduction of the  $BCl_3$  to elemental boron by  $H_2$  takes place on the surface of the hot substrate. The fiber diameter increases as the substrate travels through the tube, and the diameter of the fiber emerging from the bottom electrode and mercury seal

TABLE 3.4 Comparative Properties of Reinforcing Fibers

| Fiber          | Density | Average<br>Tensile<br>Strength<br>ksi | Modulus of<br>Elasticity<br>msi | Approximate<br>Cost<br>\$/lb |
|----------------|---------|---------------------------------------|---------------------------------|------------------------------|
| Boron, 4 Mil   | 2.57    | 620                                   | 60                              | 400                          |
| Boron, 5.6 Mil | 2.49    | 520                                   | 60                              | 400                          |
| Carbon         | 1.75    | 450                                   | 32                              |                              |
| E-glass        | 2.54    | 490                                   | 10                              | 2.5                          |
| Aramid         | 1.44    | 520                                   | 18                              | 20                           |
| SiC, 5.6 Mil   | 3.0     | 570                                   | 80                              | 2500                         |

is a function of the fiber throughput rate, other reactor parameters being constant. The boron fiber is wound onto an 8-inch diameter take-up spool.

During the course of the deposition reaction, the tungsten substrate wire is reacted to form a mixture of tungsten borides, expanding in diameter to about 0.7 mil. The internal stress states in the fiber set up from this core expansion and simultaneous boron mantle deposition are key factors in determining the ultimate tensile strength of the fiber.

The typical surface appearance of the boron fiber is that of a corncob structure (see Figure 3.12). The crystallite size, on the order of 20 Å is so small that it is considered amorphous.

The average tensile strength of high-quality boron fiber is the statistical result of many individual fiber tests; a typical histogram depicting these results is shown in Figure 3.13. Note that a comparatively low strength "tail" is present, related to various defects that can lead to premature failure of an individual fiber segment during a tensile test. Much higher test values for boron fibers of up to  $10^6$  psi can result from smoothing the surface by chemical etching or, especially, by removing the fiber core. However, neither practice is routine in boron filament processing. The costs of boron filament are mainly associated with the boron trichloride, the substrate, and capital equipment. While the cost of boron trichloride and substrate would decrease drastically if made in commodity quantities, it is unlikely that this will happen. Hence, while it is conceivable that boron filament could be produced for much less than \$100 per pound, the present prices of several hundred dollars per pound are dictated by the current costs for boron trichloride and the substrate.

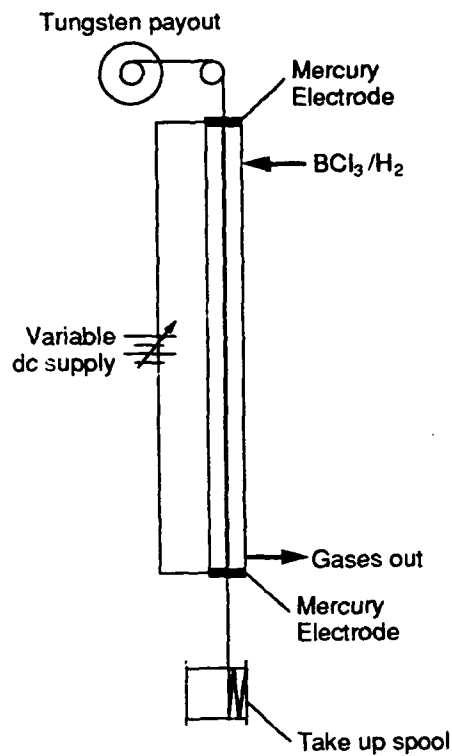


FIGURE 3.11 Boron Filament reactor.

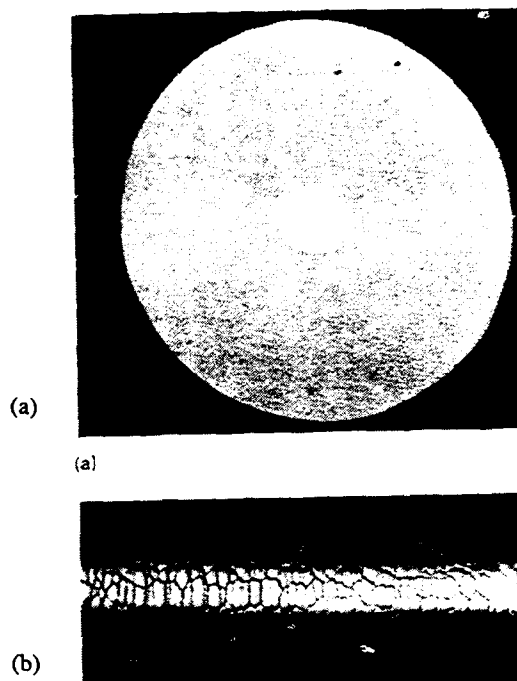
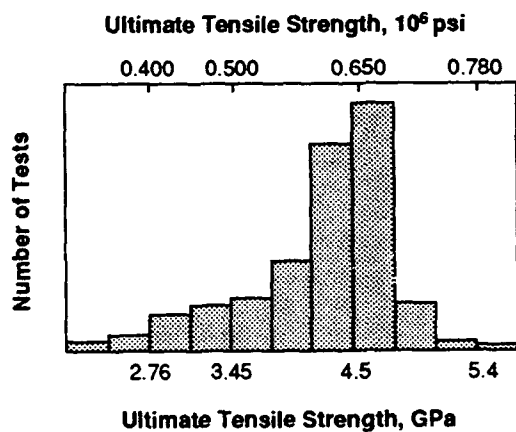
FIGURE 3.12 Photomicrographics of boron fiber (a) filament 100- $\mu\text{m}$ . core. 560 x. (b) Magnification of boron filament surface 110x.

FIGURE 3.13 Histogram of boron fiber tensile strength.

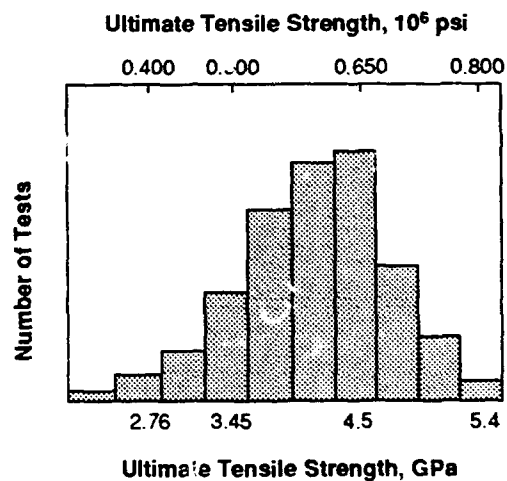


FIGURE 3.14 Histogram of CVD SiC fiber tensile strength.



### Silicon Carbide Fibers

SiC continuous monofilament is produced in both 5.6-mil and 3-mil diameters by TEXTRON Specialty Materials, and in a 4-mil diameter by British Petroleum. A typical histogram of strength properties for 5.6-mil SiC is shown in Figure 3.14.

Almost all of the SiC fiber now produced is used in development programs for reinforcing metal alloys of aluminum and titanium compositions. It has also been used successfully to reinforce organic and ceramic matrices. The 5.6-mil variations of silicon carbide fiber produced by TEXTRON are SCS-2, which is designed for reinforcing aluminum alloys; SCS-6, which is used to reinforce titanium alloys; SCS-8, which is used to reinforce an aluminum alloy structure when the composite must display higher transverse properties than can be obtained by using SCS-2; and SCS-10, which has a surface coating for titanium alloys and is produced by a new process considerably less complex than that used for the other variations. Three-mil SCS-9, intended predominantly for National Aerospace Plane (NASP) applications, is also made using the simplified reactor scheme.

The fiber is formed from the reaction of hydrogen with a mixture of chlorinated alkyl silanes at the surface of a resistively heated carbon substrate. One of the main attractions of SiC fiber is its potentially low cost, but it is currently priced at about 25 hundred dollars per pound. Projections for volume production levels that are roughly equivalent to present boron production rates indicate that a cost less than that for boron is achievable. The explanation for this cost reduction resides in the lower costs of the substrate and raw materials for SiC production, along with higher reaction and deposition rates than for boron.

There is a major difference between using fibers to reinforce metallic structures and using them to reinforce organic or ceramic matrices. A high degree of compatibility at the fiber-metal interface is essential for the benefit of the reinforcement properties to be exhibited in the composite. However, if the degree of affinity between the fiber and matrix is too high, the reaction between the metal and the fiber at the interface will result in a severe degradation of fiber properties such that a strong composite will not result.

In general, a chemical vapor deposition (CVD) fiber being used to reinforce a particular metal structure will probably not be a monolithic multipurpose fiber, but will more likely be a specialized material having a surface composition specifically selected for the particular matrix. For SiC fiber the significance of this is displayed in the SCS fiber series, which differ only in the gradations of surface composition. In all cases the bulk fiber consists of polycrystalline  $\beta$ -SiC of much larger crystalline size than in the case with boron fibers. Thus, while the bulk of the fiber is the same, each of these fibers is produced with a different carbon-rich zone near the surface. The differences among the fibers reside in the respective values of the Si/C atomic ratio and the fineness of the grain structure as a function of fiber radius in this several-micrometer-thick surface zone.

### CVD Carbon Fibers

In addition to the above methods for producing fibers by CVD onto a premanufactured substrate fiber, there are methods for producing fibers by insitu growth of the substrate fiber followed by a CVD step to produce a fiber having the desired composition. The predominant fiber that has been produced by this method is carbon. The driving force for development of this fiber has been the potential of lower manufacturing cost when compared to conventional carbon fiber manufacturing techniques. The use of these fibers is envisioned to be limited to secondary structural applications where discontinuous randomly oriented reinforcement can be employed.

### TECHNICAL FUTURE

Boron fiber is a relatively mature product; boron-epoxy composites are in production use on F-14, F-15, and B-1B aircraft. Tens of thousands of pounds of boron-epoxy composites are also currently being used in sporting goods applications. Potentially large applications for boron in the future reside in boron-aluminum composites for electronic packaging materials for airborne applications, as repair materials for civilian and military aircraft, and for aeroshells for penetrating weapons for armor or earth structures.

A production-scale application for silicon carbide fiber reinforced composites has yet to be demonstrated. However, successful tests of SCS-8 aluminum composites have been achieved in a development and test program for military aircraft sections, which has encouraged moves toward larger-scale engineering development. NASP applications could call for over 20,000 lb of SiC fiber in composites, as well.

In general, the development of production CVD fibers has involved a high degree of engineering empiricism with regard to both processing methods and design of the fiber products themselves. This approach has resulted in complexity of processing methods and belated attention to important questions—for example, strength retention at elevated temperatures, matrix interactions during consolidation heat treatments, and internal stress structure in the fiber and its effect on composite performance under realistic stress and fabrication conditions. A basic science approach to these and other problems has, in general, been lacking.

### Observations and Conclusions

- CVD fiber for advanced applications will probably not be a multipurpose fiber, but will more likely be a specialized material having a tailored surface composition specifically aimed at matrix compatibility.

- Application of an appropriate surface coating on existing fiber can markedly enhance its stability relative to either the matrix composition or to thermal and environmental conditions that the composite is subjected to during fabrication or service life.

■ A basic science approach to the CVD fiber-formation process, providing fundamental insights into decomposition kinetics, fiber-formation mechanisms, and surface reactions, can result in a better optimization of processes and products. Although it may not be inordinately difficult to form a new CVD fiber of a given composition initially, achievement of consistency in properties may require understanding and carefully controlling the parameters of the deposition process.

### Single-Crystal Fibers

One of the main deficiencies of currently available ceramic fibers is creep at high temperatures. Above  $\sim 1100^\circ\text{C}$  the structure of polycrystalline  $\text{Al}_2\text{O}_3$  and  $\text{SiC}$  fibers changes, causing slippage along grain boundaries, which greatly impairs the physical properties of the fiber.<sup>36</sup> Many of the mechanisms responsible for high-temperature creep, such as grain growth and slippage at grain boundaries, can be eliminated through the use of single-crystal fibers. Single-crystal fibers can be produced by many different techniques, such as growth from solution, melt, and vapor phases. Production of such fibers at the present time is being performed primarily by three techniques: controlled drawing from the melt, vapor growth, and zone refining.

#### *Controlled Drawing from the Melt*

This process is a variation of the Czochralski<sup>37</sup> method for producing single crystals. In this technique a single fiber is slowly drawn from a pool of molten ceramic material. Since the ceramic materials melt around  $2000^\circ\text{C}$ , extremely high temperatures are employed. One of the major problems in Czochralski growth is the presence of thermal convection in the melt pool, which causes local temperature fluctuations and increases the probability of nucleation of multiple crystals. The cooling rate of the fiber as it is drawn from the melt must also be carefully controlled to prevent the nucleation and growth of multiple crystals within the fiber. Thus, while controlled drawing from the melt using classical Czochralski techniques can be used for producing single-crystal fibers, the slow growth and the requirement for long-term stability make it likely that any fibers produced by this method will be extremely expensive.

Most recently, a variation of the Czochralski technique called the micro-Czochralski ( $\mu\text{-CZ}$ )<sup>38,39</sup> has been reported that significantly increases the speed at which single-crystal fibers can be pulled from the melt. The  $\mu\text{-CZ}$  method essentially minimizes the effects of convection in the melt by replacing the large melt crucible with a tiny heater that is wetted by the melt (Figure 3.15). The melt forms a film over the heater surface that is small in volume and which suppresses thermal convection. The single-crystal fibers are pulled from small microprotuberances on the surface of the heating element. Using this technique,  $\text{LiNbO}_3$  single-crystal fibers have been pulled at rates of 0.4–1.0 mm/s. One of the most interesting aspects of this technique is the potential for pulling multiple fibers and hence increasing the throughput of the process and possibly decreasing fiber production costs.

### Vapor Growth

In addition to the above method for producing single-crystal fibers, there are methods for producing fibers (whiskers) by insitu growth of the substrate fiber followed by a CVD step to produce a fiber having the desired composition and diameter. The predominant fiber that has been produced by this method is carbon.<sup>40-43</sup> The driving force for development of this fiber has been the potential of a lower manufacturing cost<sup>44</sup> when compared to conventional carbon fiber manufacturing techniques.

The process is illustrated in Figure 3.16. A substrate fiber is produced by exposing a small (10-30 nm) metal particle ( $\gamma$ -Fe) to a flowing mixture of a hydrocarbon gas ( $\text{CH}_4$ ,  $\text{C}_6\text{H}_6$ , etc.) in hydrogen at temperatures on the order of 900 to 1100°C. The metal particle becomes supersaturated with carbon and precipitates a cylindrical carbon tube typically on the order of ~300 nm in diameter. This tiny fiber grows in length at rates of about 1-10 mm/min. The length of the fibers is a function of the exact process conditions, but fibers have been grown to at least 30 cm. After these tiny-diameter fibers have been grown, their diameter is increased to macroscopic dimensions (about 1-10  $\mu\text{m}$ ) by CVD. The end product is an inextricably tangled mass of discontinuous carbon fibers. The individual fibers in this mass as prepared have been shown to exhibit mechanical properties comparable to those of medium-strength PAN-based carbon fibers.<sup>44</sup> After high-temperature heat treatment, the fibers develop Young's modulus on the order of 600-800 GPa comparable to those of high-temperature, heat-treated, pitch-based carbon fibers. Some vapor-grown fibers when heat treated to intermediate temperatures have exhibited a benign sword-in-sheath mode of failure in which the central core of the filament pulls out of the outer CVD sheath.<sup>45</sup> Fibers that have failed in this manner have been shown to recover a fairly large fraction of their modulus and load-carrying capability provided that the central core has not been completely removed from the outer sheath. The heat-treated CVD carbon fibers also exhibit the highest levels of thermal conductivity that have been observed in carbon fibers,<sup>46</sup> due to the high degree of perfection of the graphite crystal structure achieved in these fibers.

Whiskers of SiC have been produced by the vapor-liquid-solid (VLS) process,<sup>47</sup> which is somewhat similar to the vapor-phase carbon fiber process described previously. The VLS process is illustrated in Figure 3.17. A solid catalyst particle is placed in the growth reactor and exposed to the reactive gases  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{SiO}$ . The particle becomes saturated with Si and C and forms a molten (liquid) ball that mediates the growth of the whisker through the liquid-solid interface. The crystal grows by precipitation from the supersaturated liquid. The growing crystal is fed from the vapor by reaction of the constituent molecules at the vapor-liquid interface. Beta-SiC whiskers having tensile strengths of over 8.4 GPa and Young's modulus of 581 GPa have been reported.<sup>48,49</sup>

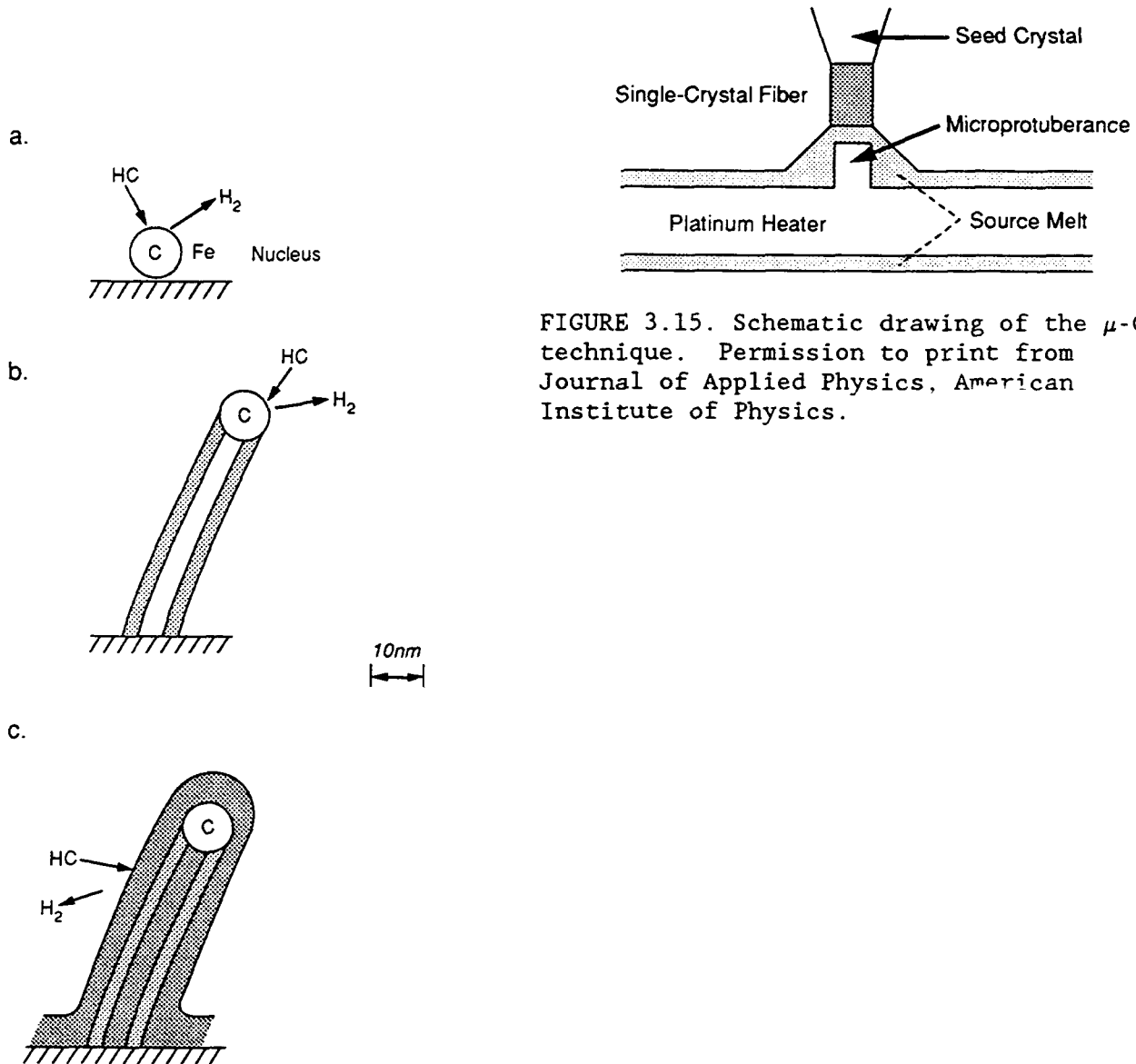


FIGURE 3.15. Schematic drawing of the  $\mu$ -CZ technique. Permission to print from Journal of Applied Physics, American Institute of Physics.

FIGURE 3.16. Description of the production of vapour-grown fibres. (a) During the saturation phase an iron particle is loaded with carbon from the gas phase. (b) A carbon filament then precipitates and lengthens as more carbon is supplied by the gas phase. (c) Finally, the filament is thickened by vapour-deposited carbon. (G. Tibbets, C.P. Beets, M. Endo., SAMPE Journal 22, 1986, p.30). Reprinted by permission of the Society for the Advancement of Material and Process Engineering.

SiC whiskers are produced on a commercial scale via the pyrolysis of rice hulls, which inherently have a high Si content. The growth mechanism for SiC whiskers produced by this method has been shown to be a variant of the VLS process,<sup>50</sup> thus illustrating that such whisker growth processes can be carried out on a small scale with economics<sup>51</sup> that are acceptable for small speciality applications.

#### *Single Crystal Growth/Zone Refining*

One of the most versatile methods for producing single-crystal fibers is the laser-heated pedestal growth (LHPG) technique.<sup>52</sup> This is a variation on the float-zone pedestal growth process.<sup>53</sup> In the LHPG technique a source rod having the desired composition is heated by a laser focused onto one end of the rod, creating a molten zone from which the fiber is pulled (see Figure 3.18). The process does not employ a crucible, the position of the laser-heated zone being fixed in space while the source rod is translated into the laser beam at a rate necessary to conserve the melt volume. One of the principal advantages of this process is the ability of the laser to produce extremely sharp temperature gradients ( $\sim 1000^\circ\text{C}/\text{cm}$ ). The steep temperature gradient combined with the high surface-to-volume ratio of the fibers causes the fibers to cool very rapidly. This helps to suppress high-temperature, solid-state-phase transformations, which can be important for stabilizing metastable forms of the material for nonstructural applications. Another of the major advantages of this technique is the complete absence of hot furnace elements that can cause contamination of the fiber.

### ALTERNATIVE PROCESSES

Processes emphasized earlier in this chapter have been found to be useful for the fabrication of high-performance fibers over a wide range of compositions. It is important to stress, however, that these processes represent only a select few chosen on the basis of demonstrated applicability. Other processes may also be useful in the development of new or improved fibers and for large-scale manufacturing. Fused composition processes such as in the traditional fabrication of glass filaments should not be forgotten. Commercial high-purity quartz yarn, used in dielectric composites, is made in France and the United States by drawing filaments from a melt fed by quartz precursor rods. Fusion and controlled spinning of some compositions, especially oxides, may be useful in the fabrication of some high-performance ceramic fibers. The "relic" process,<sup>2</sup> wherein porous fugitive organic fibers are impregnated with inorganic solutions followed by drying and pyrolyzing so as to form ceramic fibers, should be recalled. Fibers made by this process are not generally considered useful for reinforcement of composites, but determined efforts to control the microstructure of the resultant fibers should not be automatically dismissed as an impossible task. Metallic fibers may have high strengths and high modulus of elasticity values. Very small metal fibers with diameters of about  $10\text{ }\mu\text{m}$  or less have been prepared by drawing heated metal wires encased in a sacrificial sheath (e.g., glass) that is removed.<sup>1</sup> Metallic fibers, though handicapped in most cases by high-

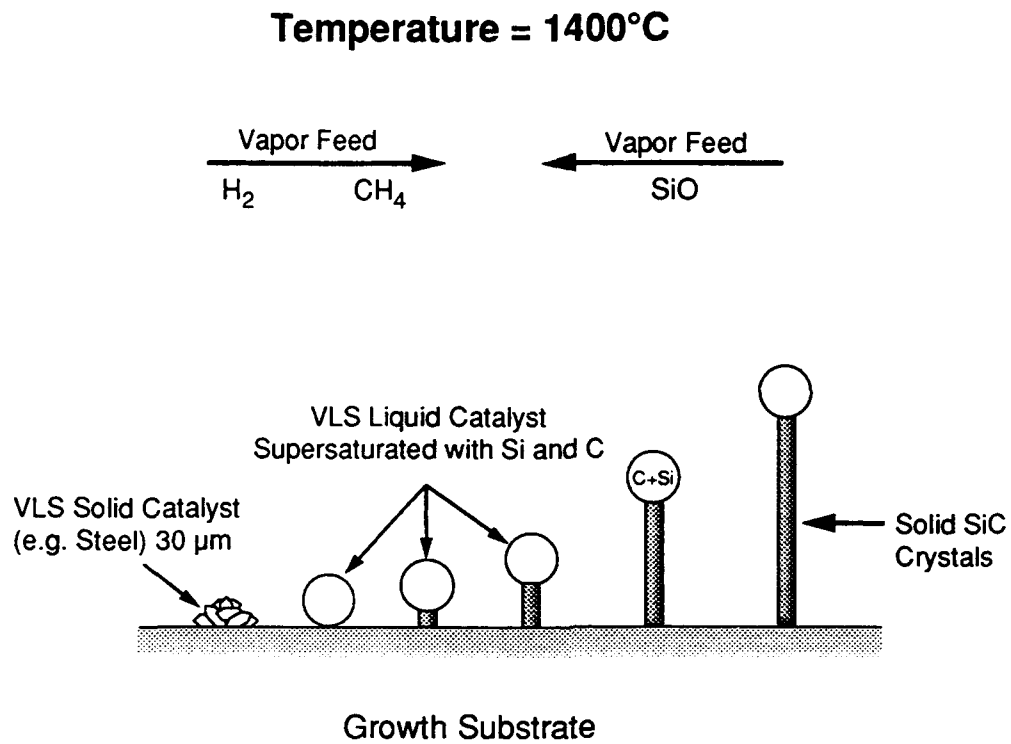


FIGURE 3.17. Illustration of the VLS process for SiC whisker growth. Permission by Journal of Materials Science, Chapman and Hall Ltd. Scientific, Technical & Medical Publishers.

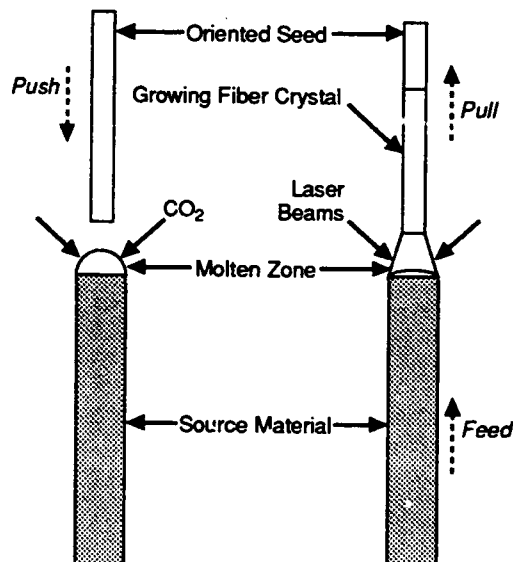


FIGURE 3.18. A Schematic diagram of the pedestal growth method. Permission to print by Materials Science and Engineering, Switzerland.

density values, may provide useful properties for special applications. Other processes are expected to be discovered or exploited as the markets for high-performance synthetic fibers evolve.

## FIBER COATINGS

### Introduction

As composite material systems become increasingly sophisticated to meet ever-increasing performance requirements, it has become necessary to develop more advanced methods for controlling the manner in which the reinforcing fibers interact with the matrix material. This is especially important in the ongoing efforts to develop high-strength, damage-tolerant ceramic-matrix composite materials<sup>54</sup> that have higher-temperature capabilities, such as for use in high-temperature regions of turbine engines. Since there are a limited number of available types of fibers that have the requisite properties for high-temperature applications, it has become necessary to develop coatings and surface treatments that facilitate the use of these fibers in an ever-widening selection of matrix systems. The application of a coating to the fiber surface is one of the most versatile methods<sup>55-56</sup> for controlling the fiber-matrix interaction. Other methods include providing additional elements to the matrix that will either form precipitates that segregate at or react with the fiber surface during fabrication and in situ modification of the fiber surface during fiber manufacturing. In this section fiber coatings will be emphasized.

Coatings offer the possibility of tailoring the fiber-matrix interfacial properties so that optimum composite properties can be achieved. Fiber coatings can have a profound effect on the composite material at all stages of its existence from fabrication to in-service use. Fiber coatings perform the following general functions:

- Control fiber-matrix bond strength.
- Improve strength by reduction of surface stress concentrations.
- Alter the wettability of fibers by the matrix.
- Improve the chemical compatibility with the matrix.
- Provide diffusion barriers.
- Protect fibers from damage during consolidation and fabrication.
- Protect the fiber and fiber-matrix interface from environmental degradation during service.

### Technical Description

There are many different methods for applying coatings to fibers. The most frequently used techniques include electrodeposition, CVD, metallorganic coating, polymer precursor coating, and line-of-sight vacuum deposition techniques. Each of these coating methods is discussed in the next section.



## Electrodeposition

Electrodeposition has proven to be one of the most convenient methods for applying metal coatings to fibers. Electroplating is used for depositing metals onto conducting substrates such as carbon fibers. In the electroplating process, continuous fibers are pulled through a plating solution while an electrical bias is applied between the fiber, which usually serves as the cathode and an anode structure in the plating bath. Figure 3.19 shows a schematic of a fiber electroplating process. During this process the fiber passes through several plating baths to build up the desired thickness of metal. The process provides good penetration of the fiber tow and usually results in uniform coating thickness.

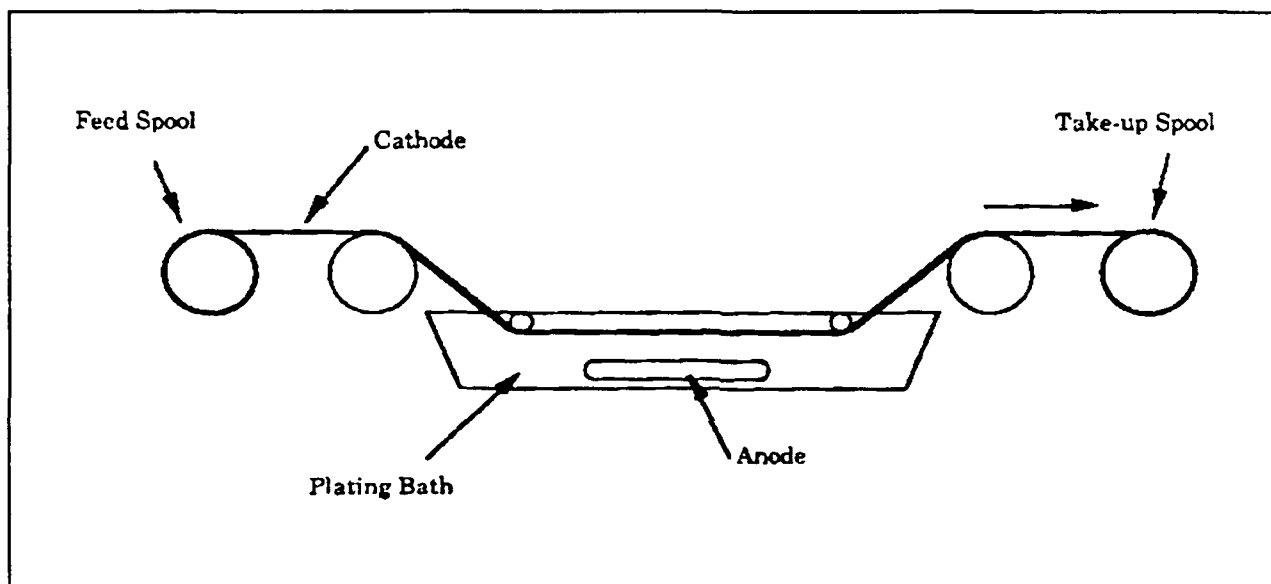


FIGURE 3.19 Schematic view of a continuous fiber electroplating process.

Although electroplating is a mature science, there are still many unresolved problems, such as determination of the composition of the plating solution that gives the highest-quality coating. For example, many plating solutions contain additional chemicals that modify or enhance the interaction of the depositing metal with the fiber surface; the scientific basis of understanding is not well developed. Electroplating is practiced commercially by American Cyanamid for coating Ni and, until recently, Cu onto carbon fibers. The major disadvantages are the limitation to metal compositions, recovery of the unused metals salts, and disposal of the waste solutions.

Methods have also been developed that permit electroplating on nonconducting fibers. These methods usually employ electroless plating to deposit a very thin conducting layer prior to entering the electroplating process. Electroless plating also has been used by itself for depositing metals on nonconducting fibers. Electroless plating is a chemical process that utilizes a surface-catalyzed reaction to deposit metal onto the fiber

surface. This method usually requires a pretreatment of the fiber to activate the surface before entering the plating solution. The major disadvantage of this process is the time required for the reactions to occur, which limits the throughput of the process.

### *Chemical Vapor Deposition*

Chemical vapor deposition (CVD), previously discussed as a method of fiber synthesis, is also used for coating. It can be broadly defined as a materials synthesis method in which the constituents of a gaseous phase react with one another and with the substrate surface to produce a solid film having the desired composition on the substrate. It is most favorable that the reactions be heterogeneous, that is, occur at the substrate surface. This usually results in high-quality films that adhere well to the substrate. If the reactions are homogeneous and take place in the gas phase, the resulting films exhibit poor properties and adhesion as a result of the formation of solid particles in the gas that eventually contact the substrate surface producing a film.

The heterogeneous reaction can be viewed as a sequence of events, any one of which can be rate limiting. The growth of a film via a heterogeneous process can be viewed as a sequence of the following processes:<sup>57</sup>

- Transport of the reactants to the substrate surface via diffusion.
- Adsorption of the reactants on the substrate surface.
- Surface processes—reaction, surface diffusion, diffusion in the substrate.
- Desorption of volatile reaction products.
- Transport of the products away from the substrate surface.

A schematic view of these processes is shown in Figure 3.20.

The different regimes in which each of these processes may become rate limiting will be controlled by the process variables—the partial pressures of the reactants, the substrate temperature, and the flow rate through the reactor. A diagram of a typical CVD reactor for continuously coating fibers is shown in Figure 3.21. The great flexibility and inherent simplicity make the CVD process one of the most widely used methods for applying coatings to fibers. The process is naturally suited to applying coatings in a continuous manner, and since the deposition is carried out in a regime in which the deposition is gas-phase diffusion limited, all of the fibers in a tow become uniformly coated. In addition, there are usually several sets of reactions that can be utilized for producing a particular coating composition. For example,  $\beta$ -SiC coatings have been produced by CVD from many different gaseous mixtures such as  $\text{SiH}_4$ ,  $\text{C}_3\text{H}_8$  and  $\text{H}_2$ , or  $(\text{CH}_3)_3\text{SiCl}$  and various hydrocarbons<sup>58</sup> as well as others. Table 3.5 gives a brief listing of materials that have been deposited using CVD processes. For a discussion of many more compounds and metals that have also been deposited, the reader is directed to more extensive reviews.<sup>59</sup> For each given set of reactants, the most crucial parameter is the substrate temperature because it determines the rate and the overall thermodynamic outcome of the reaction.

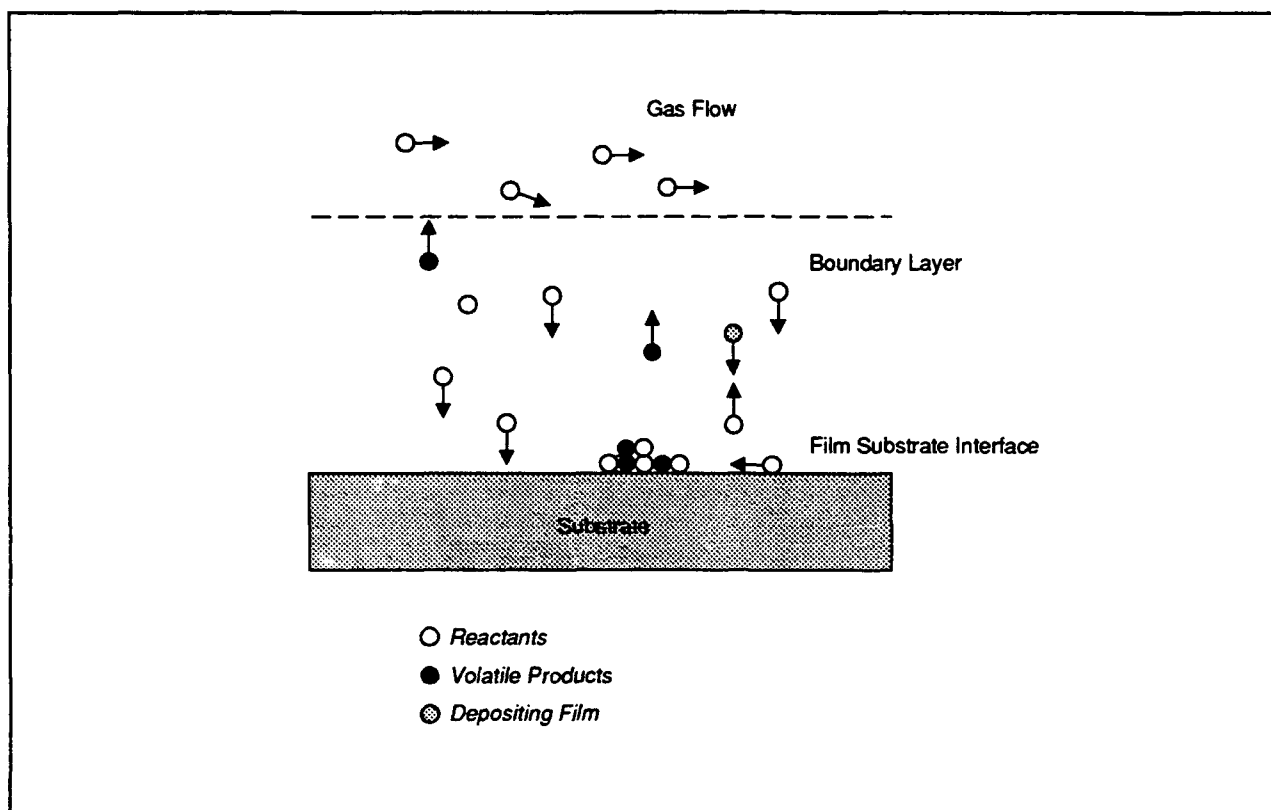


FIGURE 3.20. Schematic Diagram of the CVD Process. Permission to print by the Electrochemical Society, Inc.

Coating thicknesses from a few nanometers to a few hundred micrometers can be deposited; however, because deposition rates are slow, process throughput falls off for thick coatings. Typical deposition rates can range from  $\sim\mu\text{m/hr}$  to  $\sim 100 \mu\text{m/hr}$ . In many instances of materials having slow deposition rates, it is necessary to have multiple deposition stations along the fiber line.

#### *Metallorganic Deposition*

Metallorganic deposition is an entirely nonvacuum technique for the preparation of thin films. In this process a liquid precursor that contains a metallorganic species dissolved in an organic solvent is deposited onto the substrate surface. The substrate is then subjected to drying and heating steps that result in removal of the solvent and decomposition of the organometallic compound to produce the desired coating. The process is shown schematically in Figure 3.22. Typical precursors are metal alkoxides, metal deconates, neodeconates, and preceramic oligomers or polymers. In the case of the metal alkoxides, after the metallorganic is deposited, it is subjected to a hydrolysis reaction to convert the coating to the oxide. The remaining heat treatments then serve to remove any remaining organic residues. This process usually produces coatings that are 50 to 200 nm thick after the heat treatment stage. The process is capable of applying graded compositions by using multiple dipping stations, each having a slightly different composition.

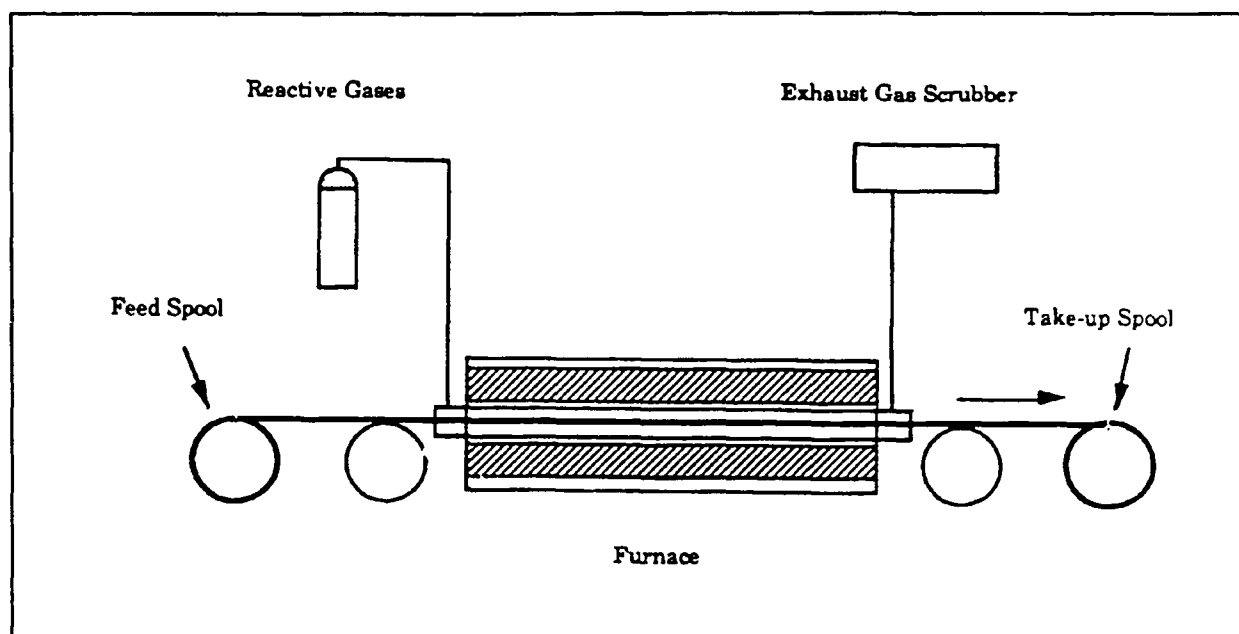


FIGURE 3.21. Schematic of a continuous CVD fiber-coating line.

TABLE 3.5 Materials Produced by CVD Processes

| CVD Material            | Reference |
|-------------------------|-----------|
| $\text{Al}_2\text{O}_3$ | 60        |
| B                       | 61        |
| $\text{B}_4\text{C}$    | 62        |
| HfC                     | 63        |
| SiC                     | 64, 65    |
| $\text{Si}_3\text{N}_4$ | 66        |
| $\text{TiB}_2$          | 67        |
| TiC                     | 68        |
| ZrC                     | 69        |

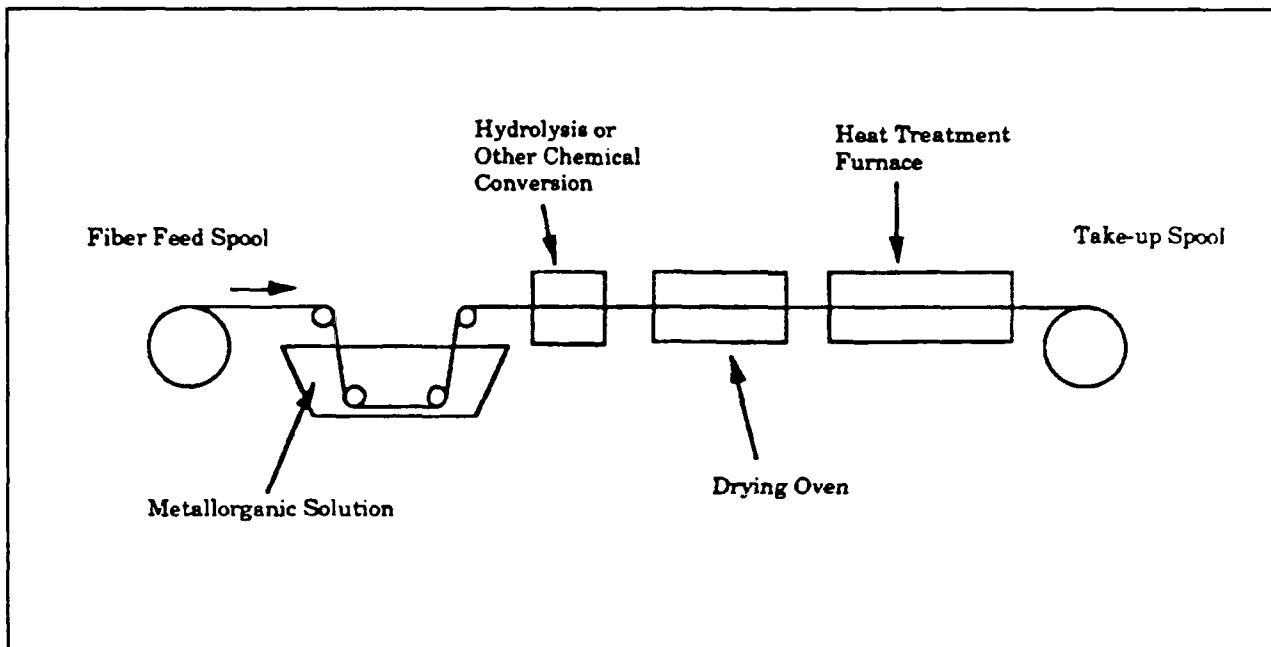


FIGURE 3.22. Metallorganic deposition process.

The process has been used most frequently to apply oxide coatings such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and mixtures of various oxides. Metal deconates undergo a similar process, but the hydrolysis step is not necessary. Preceramic polymers such as polycarbosilane, which results in  $\text{SiC}$ , are applied in the same manner as the alkoxides, but as in the case of the metal deconates, the hydrolysis step is not needed. The major disadvantage of the preceramic polymer coating method is the lack of a wide variety of coating materials. Metallorganic deposition shares many common features with electrodeposition in that the process is continuous and all operations are carried out at atmospheric pressure. The major disadvantages of this coating method are that the coating thickness for a single pass is often too thin and thicker coatings put on using multiple passes often develop cracks at the interfaces between layers.

#### *Vacuum Deposition*

This category of fiber coatings includes sputtering, physical vapor deposition, e-beam evaporation, plasma-assisted CVD, and ion-plating techniques. With the exception of the plasma and ion plating, these processes are line-of-sight deposition techniques, making deposition of uniform film on a multifilament tow very difficult to achieve due to shadowing effects by other filaments in the tow. The film deposition rates are usually slower than with CVD methods, and hence the throughput of these processes is limited. Vacuum deposition techniques for continuous filaments are at an early state of understanding, and much more work in this area needs to be done.

### Future Fiber-Coating Technology

As the demand for structural materials that can operate at higher temperatures increases, it is imperative that a thorough understanding of the role of fiber coatings be developed. Given that there is a limited set of existing fibers that can be utilized at elevated temperatures, and that these fibers are usually unstable either relative to the matrix material or the environment during fabrication of the composite or in-service use, it becomes necessary to consider the use of coatings as a means of moderating the interaction of the matrix with the fiber.

In the introduction to this chapter it was pointed out the fiber-coating matrix is a complex thermochemical-thermomechanical system and that a substantial amount of analysis is required to determine the optimum composition that a coating or series of coatings should have in order to keep the coating from interacting too strongly with either the fiber or the matrix. Currently, the best models available are thermodynamic chemical equilibrium calculations used to predict whether two compositions might react with one another under a given set of conditions to form a more stable series of products. These calculations usually do not take into consideration the kinetics of the reactions. It also needs to be pointed out that in many instances the coatings applied by the methods discussed are not ideal in that they may not be stoichiometric, or crystalline, and that if they are crystalline may contain defects or impurities that will play an important role in how the coating reacts with the fiber and surrounding matrix.

When coatings are applied at temperatures well below that of the melting point of the coating material, as is the case for most of the coating methods discussed here, the coating can be in a metastable state. On subsequent exposure to high temperatures, it will evolve toward the thermodynamic equilibrium state, possibly producing precipitates and/or reacting with the fiber or matrix. In general, there is a need for better understanding of the coating process, so that coatings result that will have the desired stoichiometries and structure. This requires development of more useful in situ diagnostic probes for monitoring the coating process to ensure uniformity of coating properties. It is highly likely that ternary and quaternary coating systems will need to be developed, and this will require a closer relationship between synthetic chemistry for the design of organometallic molecules and the film growth community for developing new methods for coating fibers with compositionally complex systems. There is also a need for techniques to evaluate the effect of the coating on the interfacial bonding properties in the composite that relate to the structure and chemistry of the interface.

### Considerations Involved in Scale-up of Fiber Processing

The processing of bulk materials into fibers is a broad-based technology that is relatively well understood in principle. However, scale-up of fiber processing is more difficult than that of other materials because of the simultaneous heat, momentum, and mass transfers, combined with chemical reactions and unique, complex, flow-induced orientation effects. Fiber

process development may conveniently be divided into three levels of detail and complexity, namely: feasibility, screening, and end-use evaluation.

Demonstration of the feasibility of converting a given bulk material to fiber involves converting a minimal amount of the bulk material to a short length of fiber and a gross evaluation of the mechanical, thermal, and chemical properties of the filament so produced. To do this with almost any material is relatively simple and may be accomplished with as little as a few grams. Typical methods might include "hand pulling" of a fiber from a melt or solution or the use of a single-filament microspinning machine. Fibers so produced lack physical and structural uniformity and give only the broadest insight into the spinnability and property set of the fiber obtained.

Screening involves tens to hundreds of grams of the fiber-forming precursor material (per experiment), which is spun into either a single filament or yarn with a small number of filaments using small-scale spinning equipment. This allows broad control of the key spinning variables such as temperature, stress, and mass transfer—parameters that control the structure and therefore the properties of the fiber produced. By allowing the systematic study of process-structure-property relationships, screening permits the initial evaluation of the fiber's probable utility. In screening experiments the purity and homogeneity of the precursor material start to play a major role and allow an initial characterization of the range of properties available from the material in fiber form. For example, polyethylene that is conventionally melt spun and drawn yields a modulus of around 100 g/d and a strength of perhaps 8 g/d. The same polyethylene gel spun and drawn to much higher draw ratios might yield a modulus of 2500 g/d and a strength of 30 g/d. The mere pulling of a polyethylene melt into a long thin length of material would not have given any indication that property variation over a range of several orders of magnitude was possible.

The importance of purity of the material can be illustrated by the following example. Assume a melt-spinnable material being extruded into a 20 dpf fiber at the relatively slow spinning speed of 500 m/min. If the material contains one impurity particle per 100 g capable of upsetting the spinline, a single filament spinning might run for 25 min. yielding 45,000 m of yarn for evaluation and the impression of stable spinning. If the more realistic case of 10-filament spinning is attempted, the spinline might be expected to breakdown after only about 5 min. If a 100-filament process simulation is attempted, less than 1 min of stable spinning is possible. Similarly, a parameter control upset (i.e., an anomaly in temperature or quench rate) will interrupt the spinning process and/or profoundly influence the fibers' properties. The difficulties associated with control are exacerbated as the fiber forming process becomes more complicated, and the small-scale simulation of highly complex processes, such as the production of ceramic fiber from polymeric precursors, may be essentially impossible to evaluate on a very small (100-1000 g) scale.

True end-use evaluation of process development requires large amounts (tens to hundreds of kilograms) and highly controlled, relatively large scale equipment. The equipment must be capable of 24-hour operation because only fiber data generated under steady-state conditions are meaningful. Often,

major property and processability improvements are noted in large-scale fiber evaluation because of the superior parameter control possible in large batch operation. In the case of a large-scale operation, feed material purity and homogeneity requirements are obviously high for the program to be initiated, much less successfully completed. Experiments beyond the screening stage are, therefore, nontrivial and involve the commitment of major capital resources, expertise, and man-hours.

#### OBSERVATIONS AND CONCLUSIONS ABOUT FIBER FABRICATION AND PROCESSING

- Technologies for the fabrication of a wide range of high-performance fibers are known and have been used to prepare fibers of many types with great diversity in composition and properties.

- The high cost of manufacturing remains a common problem from the standpoint of economics and utilization of many high-performance synthetic fibers.

- Pyrolysis and chemical conversion of precursor fibers, CVD, and single-crystal growth processes are promising routes to the fabrication of continuous high-performance synthetic inorganic fibers.

- The control of microstructure during fabrication and applications is a vital consideration for all classes of high-performance synthetic fibers for structural uses.

- New processes and increased understanding of the processes used now will be important in the development of reinforcement fibers for future composite applications with more demanding requirements.

- Continued efforts on fiber coating processes and fundamental studies on interfacial effects between fibers and matrices are needed.

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## IMPORTANT ISSUES IN FIBER SCIENCE/TECHNOLOGY

### INTRODUCTION: OVERVIEW OF NEEDED RESEARCH AND DEVELOPMENT

Previous chapters of this report have provided descriptions of the state of the art of high-performance synthetic fibers and have called attention to further development needs and application opportunities. This chapter discusses important factors that must be addressed in the effort to improve existing fiber systems and develop new ones for composite reinforcement. These factors, encompassing the scientific and engineering fundamentals underlying fiber preparation and property evaluation, can have a major impact on the rate of progress and success of fiber research efforts. Attention is required to the following technical issues concerning fiber characteristics and fiber-formation processes.

- Fiber science begins with systems selection. A systematic approach must be developed to identify fiber compositions and structures that ensure compatibility with the matrix material in specific applications. Inasmuch as a reinforcing fiber will be incorporated in a matrix to form a composite, the characteristics of the matrix as well as the composition of the fiber must be carefully considered. Once these compositional issues are determined, fiber formation or processing routes must be devised that will produce a uniform and consistent product for evaluation and that will lead to the lowest-cost commercial product. Fiber selection normally involves physical property extrapolations from bulk materials data supplemented by thermodynamic calculations, followed by generation and evaluation of small samples of the fiber. The problems associated with production-level scale-up must be kept in mind in evaluating the performance of small samples.

- A scientific understanding of the mechanisms involved in the formation of the fiber and of the microstructural factors affecting the fiber's properties is extremely important. The following factors must be understood: the chemical and physical processes involved in the formation of the fiber, their rates, and how these rates can be controlled for optimum throughput and

properties. Factors governing the ultimate strength of the fiber may include: surface flaws, internal stresses, internal composition gradients, substrate quality for chemical vapor deposition (CVD) fibers, or precursor quality for pyrolyzed fibers. Studies must answer these questions. Research must also reveal the optimum morphology throughout the fiber and at its surface and show how these morphologies can be achieved.

- Of particular importance is an understanding and optimization of the chemical composition and morphology of the fiber surface, given the nature of the matrix that the fiber will be used to reinforce and the conditions for incorporating the fiber into that matrix. The type of bonding required at the fiber-matrix interface will often dictate the characteristics that must be designed into the fiber surface. In addition, surface coating layers may be required to enhance the fiber strength, to act as a diffusion barrier preventing chemical attack by the matrix, or to accommodate any thermal expansion coefficient mismatch between fiber and matrix. This important issue is addressed further in the next section.

- In the development of new fibers for high-temperature applications, there is a growing need for predictive tools to guide and aid the fiber scientist in this task. Many of the envisioned applications require the materials system to meet several requirements simultaneously, such as high-temperature creep, minimum strength and modulus, and environmental resistance. However, at the present time there are no specific properties or indicators that can be reliably used to judge the suitability of a material for the proposed application.

- A critical issue for processing science is the matter of fiber evaluation. Normally, room-temperature physical properties such as strength, modulus, diameter, and density of the fiber are of major interest. Methods for determining these properties must be better defined. However, it must be recognized that there is a statistical distribution of fiber strengths instead of a single value and that strength is strongly influenced by test gage length. In addition, for high-temperature applications, the fiber properties at elevated temperatures must be optimized; therefore, in principle, tests and evaluations of high-temperature behavior should be carried out during process development. Moreover, the ultimate physical properties of the fiber must be optimized with regard for its performance in the final composite. Absence of adequate fiber test methods encompassing all these requirements obviously can have significant impact on the results and interpretations of the initial fiber-screening evaluations.

- To withstand long-term thermal cycling conditions, the composition of the reinforcing fiber must be in chemical equilibrium with the surrounding matrix. This means that the reinforcing fiber may need to contain certain chemical constituents of a given matrix to ensure the integrity of the composite or that its surface must be coated or modified to make the fiber compatible with the matrix.

■ Current research indicates a direct link between the microstructure of the fiber and the ultimate fiber properties, such as compressive strength and even sensitivity of the fiber to flaws. In the case of fibers with diameters frequently smaller than the dimensions of grains in traditional macro-sized articles, microstructures necessarily comprise relatively minuscule features, and direct comparison of their effects with those in relatively large entities may not be significant. Nevertheless, there is ample evidence that a fiber's acceptability may be determined by its microstructure. Moreover, the role of processing conditions on the development of this microstructure is poorly understood. If the full potential of high-performance fibers is to be realized, future research should be directed toward a fundamental understanding of this role as well as the relationship between microstructure and fiber properties.

#### The Fiber-Matrix Interface ("Interphase") and Fiber Coatings

In all types of fiber-reinforced composites, the region located between the fiber and the matrix is extremely important from the early stages of composite processing to the ultimate application. While often referred to as the fiber-matrix interface, this region may be of considerable thickness and volume and may be more appropriately referred to as the phase or "interphase" between fiber and matrix. Important considerations for this region are as follows:

■ The nature of the fiber surface is important in controlling initial fiber properties. In many cases it can determine handleability and control fiber strength. A classic example is the complex carbon-rich surface preparation of chemical vapor deposition-silicon carbide (CVD-SiC) monofilaments, which significantly improves fiber abrasion resistance and handleability.

■ The surface chemistry and features of the fiber are important in determining composite fabricability. In both polymer-matrix and metal-matrix composites produced by casting, the ability of the matrix to "wet out" on the fiber can be determined by the fiber surface. Well-known examples of this include the epoxy-compatible "sizings" applied to carbon and glass fibers and the Ti-B surface preparation of carbon fibers in preparation for aluminum and magnesium metal infiltration.

■ Both fabrication and service conditions are important in providing driving forces for reactions between fiber, interphase, and matrix. In general, any reaction between fiber and matrix will cause changes (usually a decrease) in the fiber's properties. This behavior has been controlled by the following:

1. Applying a coating to the fiber to prevent or minimize any reaction.
2. Creating a complex coating on the fiber that minimizes the effect of any reaction with the matrix on fiber strength and yet provides a region to stop crack propagation. A fiber of this type is the large-diameter SiC monofilament produced by Avco-Textron in the United States and shown in Figure 4.1.<sup>1</sup>

3. Allowing the fiber-matrix reaction to create an interphase region, which is helpful to the composite. With nicalon-fiber reinforced glass-ceramic composite, for example, the reaction that occurs during processing can cause an interphase that is desirable in stopping cracks (see Figure 4.2).<sup>2</sup> The reactions which create this interphase also are accompanied by a reduction in fiber strength, but this has been shown to vary based on the choice of matrix chemistry.

The link between fiber and matrix is very important in determining the properties of composites. Load transfer is accomplished from the generally lower-stiffness matrix to the high-modulus fibers through the interphase. Mechanical fiber-matrix bonding is sufficient to accomplish this transfer for axial composite properties, but highly bonded regions are necessary to achieve high levels of off-axis and shear properties. In both polymeric matrix composites (PMC) and metal matrix composites (MMC) systems it has generally been desirable to maximize the integrity and strength of the interphase region for this purpose.

Fracture control presents a more complex issue. The interphase region provides the opportunity to control the fracture process in several ways. First, strong fiber-matrix bonding can cause the dissipation of large amounts of energy during crack growth by causing extensive shear deformation in the interphase and matrix surrounding the fiber. In MMC systems this has been extremely effective. The fracture of well-bonded boron-reinforced aluminum composites has been characterized by large amounts of matrix shear (see Figure 4.3).<sup>3</sup>

Second, weak fiber-matrix bonding can also be important in the fracture control process by diverting cracks as they reach the fiber-matrix interface and during fiber pullout. While highly prominent in the discussion of CMC systems, this can also be true for MMC composites, such as that shown in Figure 4.4.<sup>4</sup> Finally, with CMCs the region separating the fiber and the matrix becomes even more important, because for maximum performance it must prevent crack propagation. In these systems the matrix may crack at rather low strains. If these cracks are diverted or interfered with, composite toughness will be enhanced and the fibers will be able to reach higher stress levels before fracturing. Thus, with CMCs the region between fiber and matrix must exhibit sufficient strength to transfer load and be weak enough to divert cracks.

#### SUMMARY OF TECHNICAL ISSUES

Progress in high-performance synthetic fibers of all types demands greater emphasis on fundamental research directed at four interdependent technical issues:

- Fiber-formation processes and mechanisms.
- The effect of fiber processing on microstructure.



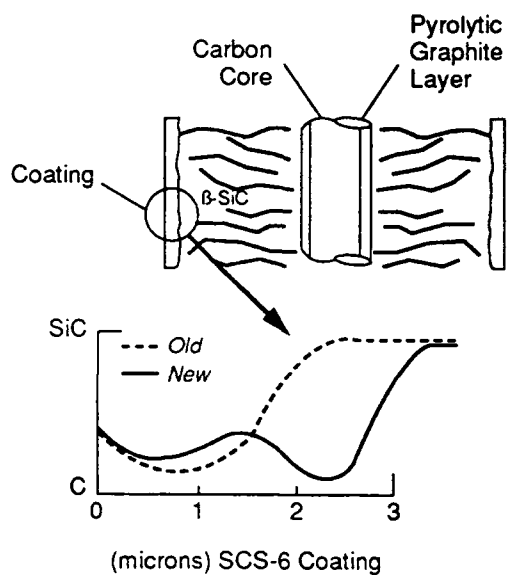


FIGURE 4.1. Structure and composition of SiC fiber produced by Chemical Vapor Deposition.

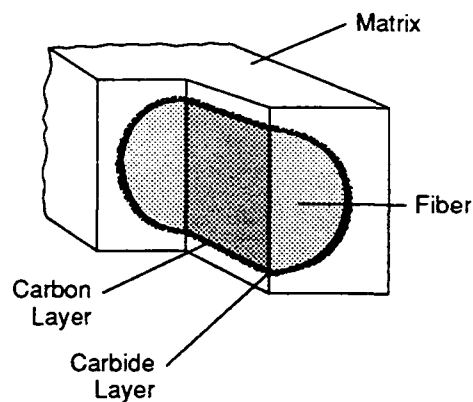


FIGURE 4.2. Interphase region produced during fabrication of Nicalon fiber reinforced glass-ceramics.

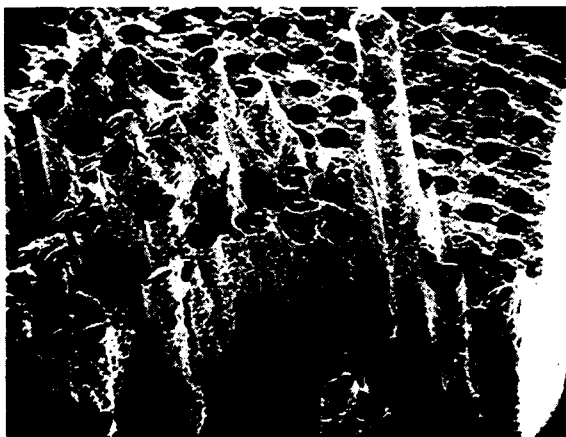


FIGURE 4.3. Fracture surface of boron reinforced 6061 aluminum with prenotched region also shown.

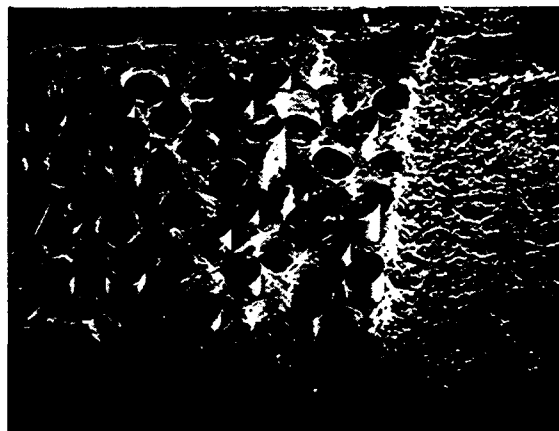


FIGURE 4.4. Fracture surface of Borsic reinforced titanium with prenotched region also shown.

- The relationship of microstructure to fiber properties.
- Fiber-matrix interfacial interactions during fabrication and in service.

A systematic approach needs to be developed, starting from the known properties of bulk material, to identify and select candidate materials for fiber development. This approach should incorporate early consideration of the matrix and potential fiber-matrix interactions during processing as well as in the service life and environment of the final composite.

Standardization of fiber characterization and testing procedures for comparative evaluation of fiber performance is highly desirable.

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## IMPORTANT POLICY ISSUES

### INTRODUCTION

It is generally recognized that the advanced composites industry is a critical industry for the United States in terms of its strategic implications for the Department of Defense (DOD); its potential to influence the U.S. balance of payments through the twenty-first century; and its practical impact on American society through the creation of new jobs and the development of improved materials for a broad range of end uses. High-performance fibers are the backbone of this industry and as such are keys to determining the ultimate success that composites will have as a replacement for metals or other materials. The commercialization cycle for these premier fibers is often long and very expensive. Because of the long development time and uncertain returns, many U.S. companies are wary of entering the field or do not have the resources to participate. The U.S. government is often necessarily involved because of the strategic nature of some of the materials and the need to control technology export. A continuing effort to develop these high-performance fibers is essential for our national security and economic well-being. To make sure that the United States stays competitive against foreign competition in this field, continuity of funding of research, development, and engineering is necessary, as is improved cooperation between university, industry, and government. As the background for this cooperation, certain policy issues require review and clarification. Some of the more critical issues are as follows:

- Education in fiber science/technology.
- Domestic sourcing considerations.
- Technology export/export control.
- Production of small quantities of specialty fibers.
- Foreign competition.
- Continuity of support.

## EDUCATION IN FIBER SCIENCE AND TECHNOLOGY

### Academic Program Development

Because of their fiber form, the complex chemistry involved in their production, and their ultimate use in materials, effective research and development of high-performance fibers must involve an interdisciplinary team of textile and materials scientists as well as ceramic, chemical, and materials engineers. Although the present supply of people trained in these individual disciplines is substantial, the curricula are somewhat dated. Future training in these fields must stress interdisciplinary interaction and must specifically emphasize oriented anisotropic materials, if the graduates are to function easily on these teams. Support for course development and seminars in these disciplines will be vital. Such interaction would expose these future engineers and scientists to the problems of other fields and would foster a spirit of interaction even prior to graduation.

### Equipment Support for Teaching and Research

Perhaps the most critical problem facing our universities is outdated equipment for teaching and research. Nowhere is this more apparent than in high-performance fiber research. The equipment available in our textile schools has been estimated to be an average, over 25 years old. Many engineering and science programs suffer from the same problem. Even where the equipment is operational, spare parts are difficult to acquire or simply out of production. If the United States is to remain competitive in fiber technology, this problem must be addressed immediately. To do so, a research initiative program, specifically directed at high-performance fiber research equipment, is proposed.

Equipment upgrading should be a part of ongoing funding. In industries involved in high-performance fiber research, many companies invest 25 percent of their research budgets in capital equipment. In the future a similar approach should be applied to federally funded proposals involving high-performance fiber research. Since most universities do not charge overhead on capital equipment, investing 25 percent of a research proposal in new equipment often can provide more effective funding for the actual academic investigator. Such an increase in the expected percentage of equipment funding in fiber research grants could rejuvenate our university laboratories and have a significant long-term effect on education in fiber science and engineering.

### Industry-University Interaction

The long-term competitiveness and health of our synthetic fiber industry will require increased interaction between the industry and our universities. While many problems encountered in high-performance fiber research and development are considered proprietary by industry, the interchange with others in the same industry and the exposure to academic viewpoints could foster increased creativity in our fiber industry. To foster this interaction for the purposes of meeting national needs, the U.S. government must advocate

and facilitate this interaction. Such contact is critical to ensure that academic research is directed toward the real problems facing the fiber industry in the United States.

#### DOMESTIC SOURCING CONSIDERATIONS

Currently, most of the generally accepted advanced structural reinforcing fibers are manufactured in the United States using domestic raw materials. These include S-2 glass, boron, aramid, pitch-based carbon fibers, and ultrahigh-strength polyethylene fibers. Two key structural reinforcing fibers, which are obtained both from domestic and non-U.S. manufacturers, are various classes of ceramics and polyarylonitrile (PAN)-based carbon fibers. Ceramic fibers are early in their commercial development and are not currently significant constituents of advanced material consumption in the United States.

PAN-based carbon fibers are probably the largest constituents and the fastest growing of the structural reinforcing fibers used in the United States. U.S. carbon fiber manufacturing capacity is currently estimated at approximately 5000 metric tons (11 million pounds [12 K basis]). At present, the domestic industry is operating at or near full capacity, and domestic supply is supplemented by sizable quantities of carbon fiber imports from Japan and the United Kingdom. Additionally, major carbon fiber capacity is expected to exceed annual domestic consumption by some margin when newly installed and expanded facilities are in full production in the early 1990s.

Despite the rather large and growing U.S. capacity for the manufacture of carbon fibers, until recently most U.S. producers purchased their precursor from overseas—Japan or the United Kingdom. As of 1989, only one carbon fiber producer (Amoco) manufactured its own precursor in the United States and its capacity was very limited. The U.S. government, considering carbon fibers as a critical material for DOD applications, believed that action had to be taken to ensure a secure supply of material in the advent of a national emergency. Thus, P.L. 100-202 was passed in 1987 requiring the Secretary of Defense to "assure that a minimum of 50 percent of the polyacrylonitrile PAN carbon fiber requirement be procured from domestic sources by 1992." As a direct consequence of the passage of this bill, all of the major U.S. carbon fiber suppliers have either built or have announced construction of domestic PAN precursor facilities. Hercules recently completed construction of its facility, and BASF is currently in the construction phase of its new facilities. Amoco is expanding capacity at its existing facility. Additionally, other smaller domestic carbon fiber manufacturers have indicated their intentions to install PAN precursor capacity in the United States some time in the future. On the surface, this method of ensuring an adequate supply of critical materials seems to be quite successful, since the capacity of domestic PAN-based precursor will be dramatically increased by 1992. Some government policy makers may believe that the domestic precursor initiative should be used as a model to protect the supply of future strategic high-

performance fibers. There are, however, a number of significant disadvantages to this type of policy, the implications of which should be clearly understood before it is utilized again.

Primarily as a result of P.L. 100-202, the largest U.S. carbon fiber producers will spend millions of dollars to establish domestic precursor capacity by the early 1990s. This large financial investment is being made with no real economic justification, since equivalent precursor is currently obtained from existing sources in Japan or the United Kingdom. Furthermore, it is anticipated that the total unit cost for precursor manufactured in the United States will be higher than the cost to purchase imported precursor owing to unfavorable economies of scale and higher capital and operating costs.

Significant financial risk is being incurred by U.S. carbon fiber producers to install capacity that cannot be economically justified and that will—in purely financial terms—place these U.S. carbon fiber producers at a competitive disadvantage to foreign manufacturers and domestic fiber suppliers that choose not to install domestic precursor. This risk is substantially heightened if major DOD programs (some of them slated to use carbon fiber produced with domestic precursor) are either significantly curtailed or threatened with cancellation. Also of some importance, additional time and millions of dollars will be expended by U.S. carbon fiber producers, fiber converters, and end users to requalify carbon fiber made from the new domestic precursor. Significant industry time and expense will be expended to requalify equivalent carbon fiber product with no new product or technological improvements. Ultimately, either the consumer (DOD or the U.S. taxpayer) or the advanced composites industry will pay the price for domestic sourcing in the form of higher carbon fiber prices or reduced profits (or increased losses) for the composites industry. Moreover, carbon fiber producers that cannot afford the cost or choose not to install their own domestic precursor capacity will be placed at a significant competitive disadvantage when competing for DOD contracts.

Despite the very specific implementation schedule stated in the 1987 bill, a number of factors caused a long delay before a detailed implementation plan was issued, leading to considerable confusion within the industry. Nevertheless, the U.S. carbon fiber industry went ahead with necessary capital outlays, taking significant economic risk by installing domestic precursor capacity on its own without really knowing the answer to two key questions: (1) the real timetable for implementation of the domestic precursor requirements and (2) the costs involved in the qualification of the new precursor plants and the responsibility to pay for the qualification. If taken to an extreme (e.g., almost total elimination/extended delay in major DOD programs), this pattern of carrying out domestic sourcing policy could put the major U.S. carbon fiber producers in an extremely uncompetitive situation.

Thus, while the domestic precursor initiative is clearly meeting its goal to have precursor capacity installed in the United States, it is not without significant consequences to the carbon fiber industry. It is for economic reasons such as the above that a number of U.S. companies have sold their carbon fiber businesses (e.g., Union Carbide, Celanese, Stackpole, Great

Lakes). If future needs for domestic sourcing occur, the PAN-based precursor initiative should not be used as a model. When domestic sourcing for a strategic product is inadequate, the U.S. government should coordinate closely with industry, government agencies, and universities to conceive an implementation plan that takes into account the economic and technological implications of the action. The ideal plan should satisfy U.S. strategic sourcing requirements, provide the opportunity for a fair economic return at a reasonable risk to U.S. industry, and encourage actions that will result in improved U.S. economic and technological competitiveness. If the situation is such that domestic sourcing cannot be accomplished without placing U.S. firms at an economic or technological competitive disadvantage versus foreign suppliers, the U.S. government should provide assistance to U.S. industry in establishing the needed domestic capacity.

#### TECHNOLOGY EXPORT/EXPORT CONTROL

Growth of the advanced composites industry is fueled by technology. Without sustained fundamental research and development, necessary improvements in the current high-performance fibers will not take place and the next generation of fibers required to support critical future applications will not be developed. The U.S. advanced composites industry has a comprehensive and broad technology base from which it can support the required process/product innovations, but it is not unique in this area. Similar technology bases exist in Western Europe and Japan, where there is an equally strong, if not stronger, commitment to support the development of high-performance fibers—witness the number of foreign multinational companies that have composites businesses both in the United States and in Western Europe (e.g., BASF, ICI, Ciba-Geigy, BP, Courtaulds). Thus, if the United States is to remain competitive on a worldwide basis, it must find a proper balance between protecting strategic technology and participating in the worldwide technology explosion in fibers and advanced composites materials. This view was recently expressed very succinctly by Edward Bursk, chairman of the Aerospace Industries Association's International Council, in testimony on behalf of the AIA before the Subcommittee on Economic Stabilization of the House Banking, Finance and Urban Affairs Committee:

The overriding issue for our industry is technology: the technological advantage we must maintain, and the technology we must be able to exchange with our allies for trade and security reasons. We need a balanced technology transfer policy which allows a two-way flow of technology between the United States and its allies. Unnecessary technology controls cause U.S. firms to lose sales and encourage foreign countries to form consortia which freeze out U.S. industry. If research and development are appropriately funded, then at the time technology is transferred, a U.S. firm should have incorporated still newer technology into its products and processes.

The United States exercises various technology export controls for national security, foreign policy, and economic objectives. These controls are implemented via Export Administration Regulations, International Traffic

in Arms Regulations, and Nuclear Regulatory Controls. Under the Export Administration Regulations, an export encompasses virtually any form of disclosure to a foreign entity, including that occurring within the United States.

While the United States and its COCOM partners are taking steps to "build higher fences around fewer products" (thus eliminating many unduly burdensome restrictions on multifarious products), advanced materials and materials processing are among the few areas that will remain heavily controlled.

A number of recommendations for ways to improve policy in this area have already been put forth. Some of the approaches that the U.S. government can use to deal with this very complex issue have already been presented by a blue ribbon panel convened under the auspices of the National Academy of Sciences to study the conflicting interests of U.S. national security export controls and global economic competition. Since completion of that study the international political, economic, and military pictures have changed dramatically, further complicating policy considerations. Although the committee believes that broad national policy recommendations on these issues are beyond its charge and competence, it wishes to emphasize that technology export and export control policies have a strong impact on the advanced fibers/composites industries—an impact that can greatly affect our national scientific, technical, and economic progress.

#### PRODUCTION OF SMALL QUANTITIES OF SPECIALTY FIBERS

Invention of a new fiber or material can be a major breakthrough or it can be a wasted asset, depending on the opportunity for commercialization. One of the most critical steps on the route to commercialization occurs after the idea conception and initial laboratory-scale feasibility demonstration. By this time researchers have gained a rudimentary understanding of the technology involved, preliminary data from the lab-scale samples has been generated, and patent applications have been applied for. The commercial potential of the product is, however, uncertain due to the lack of a sufficient quantity (about 25-to 500 kg) of material for application development and assessment. This is particularly true for high-performance, specialty fibers where the development cycle is often long, the initial opportunities are in a relatively small niche application, and the returns are uncertain. Some of the approaches that a company can follow, which range from full-scale development to termination, are as follows:

- The company is willing, on its own, to pursue the program to the next stage of development.
- The company is willing to continue the developmental effort only with support from the government, arising from government interest in the commercial production of the material.
- The company is interested in licensing the technology to other companies.



- The company decides to shelve the development due to the commercial uncertainty of the product.

Unfortunately, it is at this point that many U.S. companies drop a project because of limited financial and/or human resources. This is becoming a serious issue for U.S. competitiveness because other countries are finding ways to ensure that potential developments are fully evaluated before a decision on their ultimate fate is finalized.

A policy needs to be implemented that facilitates a more cooperative relationship between government and industry and/or between companies within an industry. With government support a company will be able to go to the next level of product development (i.e., production of small quantities of the material for further exploitation). Similar results, beneficial to the country, can also be achieved by collaborative efforts between companies in the industry.

### FOREIGN COMPETITION

The United States historically has relied heavily on foreign technology for carbon fibers, which are one of the most critical fibers used for structural reinforcements. Until recently (1990), we were still heavily dependent on Japanese precursor PAN fiber and, to a lesser extent, on finished carbon fiber. U.S. producers have continued to install additional carbon fiber manufacturing capacity, with little prodding from the government, in order to meet increasing carbon fiber sales (both military and nonmilitary). However, the government did have to become involved in forcing the issue on domestic PAN-based precursor production because of the unfavorable economics that domestic precursor manufacture (versus foreign purchase) places on the industry (see Domestic Sourcing Considerations above).

The active development of pitch-based carbon fibers in Japan, if successful, could have important long-term military and commercial implications. Development of a "low"-cost carbon fiber with good structural properties would undoubtedly lead to its widespread commercial use. It would become in effect "black fiberglass" and, depending on how low the cost, could develop sales in the hundreds of millions of pounds per year. In the absence of a domestic source, we would become dependent, once again, on foreign suppliers for a key material. The United States has a very strong carbon fiber industry both PAN-based and pitch based. Therefore, the issue is whether the government should let market forces determine who develops competitive domestic carbon fibers (or even if these are developed at all) versus some type of government incentive program to ensure a leading position for the United States in carbon fiber process/product technology. In the pitch-based, carbon fiber area, DOD is already providing incentives to U.S. industry. Under the Defense Production Act Title III program, DOD is providing for a domestic manufacturing source of 100 Msi and 120 Msi modulus pitch-based carbon fibers. Title III provides the domestic industry with incentives in the form of guaranteed purchase commitments for fiber produced under the program. Additional DOD support will be provided to the domestic

pitch-based fiber industry through a Navy Manufacturing Technology program. Under a request for proposal issued by the Navy, 120 Msi and 130 Msi modulus pitch-based carbon fibers will be developed with higher thermal conductivity for lower cost.

The United States has been dependent on a foreign source for the supply of continuous high-purity silica (quartz) yarn for high-temperature, radar transparent window applications. The DOD has conducted life-of-type buys of astroquartz yarn from the U.S. distributor of the French Saint Gobain (Quartz et Silica) product. However, to avoid foreign dependence and a potential supply problem for future acquisitions, DOD is developing a U.S. capability in high-purity quartz yarns through the Defense Production Act Title III program. Over 63,000 pounds will be produced under the program. Since Saint Gobain has now installed a U.S.-based subsidiary (Quartz Products Corp., which is now on stream with high-purity quartz fiber), competitive multiple sources are available, which will help reduce fiber cost.

Another important policy issue is that it takes a long time and a considerable amount of investment for a new structural material to become widely used in the aerospace industry. Ten to 20 years is not uncommon. Add to that the risky nature of new material development and it is not surprising that domestic private investment in the development of reinforcements for high-temperature metal- and ceramic-matrix composites has been very limited. In contrast, a number of Japanese firms, with some government support, are actively pursuing what appears to be a long-term investment strategy. This raises concerns about the source of future high-temperature reinforcements. For example, Nicalon®, which is made by Nippon Carbon, is at present one of the leading, if not the leading, ceramic-matrix composite reinforcements.

An important consideration in high-performance fiber development technology is understanding the processes used to make composites from the fiber as well as how it performs in service. A number of Japanese firms are forward integrating into intermediate material forms and finished products or are forming teaming arrangements to accomplish the same objective. This is happening to a limited extent in the United States with carbon fiber composites, but in noncarbon fiber areas it could potentially give the Japanese a significant advantage over competitors who are restricted to fiber production alone.

#### CONTINUITY OF SUPPORT

Given the magnitude of the technical challenge normally associated with the development of a new high-performance fiber, it is highly desirable that such a development effort be carried out as a continuous, uninterrupted project. The development of new fibers normally takes 5 to 10 years. Unfortunately, well-conceived and complex fiber programs are frequently funded only in an incremental manner, resulting in periodic work stoppages of hard-to-define duration. Since the work stoppages are not anticipated when the fiber development programs are bid and accepted by the funding source, serious difficulties can result in areas such as retention of key personnel for the

program and maintenance of the integrity of contractor-owned laboratory apparatus. Both issues arise in connection with the demands of other projects and in the necessity of identifying other time-chargeable work for the technical personnel involved in the suspended program. The overall result of such a suspension of activity is that when the next funding increment is received and the program starts up again, considerably more time is lost than merely the duration of the funding hiatus because of the need to reconstitute the technical team and the laboratory gear.

Many programs affected in this manner are focused on the development of new fibers and technology for applications for which the government has tight and urgent time schedules the National Aerospace Plane (NASP). As with other materials needs, the critical fiber/composites components of many urgent engineering or design programs have often erroneously been considered to be program subtasks that can be scheduled for development and delivery on a short time frame. The subordination of fiber development in this way is highly unproductive and unwise.

For all the above reasons it is strongly recommended that the issue of securing continuous and appropriate funding for such programs be addressed and resolved.

## GLOSSARY OF TERMS

|                   |  |
|-------------------|--|
| Amorphous plastic | A plastic that has no crystalline component. There is no order or pattern to the distribution of the molecules.  |
| Anisotropic       | Not isotropic. Exhibiting different properties when tested along axes in different directions.   |
| Aramid            | A type of highly oriented organic material derived from a polyamide with at least 85 mole percent of its amide linkages directly connected to two aromatic rings. Kevlar® is an example of a para-oriented aramid, and is a high-strength high-modulus fiber.  |
| Aromatic          | Unsaturated hydrocarbon with one or more benzene ring structure in the molecule.   |
| Boron fiber       | A fiber produced by vapor deposition of elemental boron, usually onto a tungsten filament core, to impart strength and stiffness.  |
| Carbon fiber      | Fiber produced by the pyrolysis of organic precursor fibers, such as rayon, polyacrylonitrile (PAN), and pitch, in an inert environment. The term is often used interchangeably with the term graphite; however, carbon fibers and graphite fibers differ. The basic differences lie in the temperature at which the fibers are made and heat treated and in the structures of the resulting fibers. Graphite fibers have a more "graphitic" structure than carbon fibers.                               |
| Carbonization     | In carbon fiber manufacturing, it is the process step in which the heteroatoms are pyrolyzed in an inert environment at high temperature to leave a very high carbon content material (about 95 percent carbon and higher). The carbonization temperature can range up to 2000°C. Temperatures above 2000°C (up to 3000°C) are often referred to as graphitization temperatures. The range of temperature employed is influenced by precursor, individual manufacturing process, and properties desired. |
| Coagulation bath  | A liquid bath that serves to harden viscous polymer strands into solid fibers after extrusion through a spinnerette. Used in wet spinning processes such as rayon or acrylic fiber manufacture.  |

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|-------------------------|---|
| Compression strength    | The ability of a material to resist a force that tends to crush or buckle.  |
| Crystalline orientation | The term crystalline applies to sections of all chemical fibers, which consist of alternate crystalline and amorphous (noncrystalline) regions. These regions are influenced by manufacturing conditions and can be controlled to some extent. Crystalline orientation implies the extent to which these crystalline regions can be aligned parallel to the fiber axis. Crystalline orientation is an important factor in determining the mechanical properties of carbon fibers. |
| Crystallinity           | The extent to which a polymer exists in a lattice structure.  |
| Damage tolerance        | In the aircraft industry, it is the ability of a structure to tolerate a reasonable level of damage or defects that might be encountered during manufacture or while in service without jeopardizing aircraft safety.   |
| E-glass                 | A family of glasses with a calcium aluminoborosilicate composition and a maximum alkali content of 2 percent. A general-purpose fiber that is used most often in reinforced plastics and that is suitable for electrical laminates because of its high resistivity.   |
| Epoxy                   | A polymerizable thermoset polymer containing one or more epoxide groups and curable by reaction with amines, alcohols, phenols, carboxylic acids, acid anhydrides, and mercaptans.  |
| Filament                | The smallest unit of a fibrous material. The basic units formed during drawing and spinning, which are gathered into strands of fiber (tows) for use in composites. Filaments usually are of extreme length and very small diameter, usually less than 25 microns (a mil). Normally filaments are not used individually.  |
| Flexural strength       | The maximum stress that can be borne by the surface fibers in a beam in bending.  |
| Graphite                | The best representation of the ideal graphitic structure is the crystal structure of single-crystal graphite, which is hexagonal in nature. In this structure, planes of honeycomb carbon hexagons are stacked very close together in an ordered parallel fashion. The typical in-plane bond length is 1.42 Å,  |

and the separation between planes is 3.354 Å. High-modulus, pitch-based, carbon fibers come very close to achieving this three-dimensional order type of structure, but it is very difficult to achieve starting with PAN-based precursors.

#### High modulus organic fibers

High-modulus organic fibers (HMOFs) are a new generation of organic fibers possessing unusually high tensile strength and modulus but generally poor compressive and transverse properties. Unlike conventional fibers that have a chain-folded structure, all HMOF fibers have an oriented chain-extended structure. One approach to producing such a polymer is to make a structurally modified, highly oriented version of a "conventional" polymer such as high-modulus polyethylene. A second approach is to synthesize polymers that have inherently ordered rigid molecular chains in an extended conformation. Examples of the latter are liquid crystalline aramids and liquid crystalline polyesters (LCPs).

#### Hybrid

A composite laminate consisting of laminae of two or more composite material systems. A combination of two or more different fibers, such as carbon and glass or carbon and aramid, into a structure. Tapes, fabrics, and other forms may be combined; usually only the fibers differ.

#### Induction furnace

In the carbon fiber process, a carbonization furnace that utilizes induction heating to eliminate the heteroatoms from the carbon fiber structure. Heat distribution is obtained by a combination of induced heat to a furnace muffle/susceptor within the induction coil and radiation from the interior surfaces of the furnace chamber in temperatures in excess of 3000°C. Sometimes an induction furnace is used in combination with a resistance furnace to achieve the desired pyrolysis temperature (i.e., the resistance furnace may be used to expose the fiber to a temperature as high as 2000°C, and if higher temperatures are required, as may be the case in graphitization, the fiber could then be passed through an induction furnace).

#### Laminate

A composite material made up of a single ply or layer or series of layers with each layer consisting of a reinforcing fiber imbedded in a matrix. Each ply or layer is oriented in a predetermined manner in order to maximize the properties of the laminate.

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|--------------------------------|--|
| <b>Liquid crystal</b>          | Liquid crystal materials are usually made up of rigid, rod-like molecules. They can become ordered in either solution or melt phase, which means that the molecules aggregate under certain conditions so that the materials are anisotropic. It is very easy to achieve high orientation with these materials during either liquid or melt extrusion, so the resulting extrudate (e.g., fiber or film) has excellent tensile properties.                  |
| <b>Matrix</b>                  | The essentially homogeneous resin or polymer material in which the fiber system of a composite is imbedded. Both thermoplastic and thermoset resins may be used, as well as metals, ceramics, and glasses.   |
| <b>Mesophase</b>               | An intermediate phase in the formation of carbon fiber from a pitch precursor. This is a liquid crystal phase in the form of microspheres, which, upon prolonged heating above 400°C, coalesce, solidify, and form regions of extended order. Heating to above 2000°C leads to the formation of graphite-like structure.   |
| <b>Microstructure</b>          | A structure with heterogeneities than can be seen through a microscope.  |
| <b>Morphology</b>              | The overall form of a polymer structure, that is, crystallinity, branching, molecular weight, etc. Also, the study of the fine structure of a fiber or other material, such as basal plane orientation across a carbon/graphite fiber.   |
| <b>Pitch</b>                   | A high molecular weight material left as a residue from the destructive distillation of coal and petroleum products. Pitches are used as base materials for the manufacture of certain high-modulus carbon fibers and as matrix precursors for carbon-carbon composites.   |
| <b>Polyacrylonitrile (PAN)</b> | Used as a base material or precursor in the manufacture of certain carbon fibers. The fiber-forming acrylic polymers are high in molecular weight and are produced commercially either by solution polymerization or suspension polymerization. Both techniques utilize free-radical-initiated addition polymerization of acrylonitrile and small percentages of other monomers. Commercial precursor fibers are more than 90 percent acrylonitrile based. |

|                                  |   |
|----------------------------------|---|
| Polyamide                        | A thermoplastic polymer in which the structural units are linked by amide or thio-amide groupings (repeated nitrogen and hydrogen groupings).   |
| Polyamideimide                   | A polymer containing both amide and imide (as in polyamide) groups; its properties combine the benefits and disadvantages of both.  |
| Polyester<br>(Thermosetting)     | A class of resins produced by dissolving unsaturated, generally linear, alkyd resins in a vinyl-type active monomer such as styrene, methyl styrene, or diallyl phthalate. The two important commercial types are (1) liquid resins that are cross-linked with styrene and used either as impregnates for glass or carbon fiber reinforcements in laminates, filament-wound structures, and other built-up constructions, or as binders for chopped-fiber reinforcements in molding compounds; and (2) liquid or solid resins cross-linked with other esters in chopped-fiber and mineral-filled molding compounds. |
| Polyether ether ketone<br>(PEEK) | A linear aromatic crystalline thermoplastic. A composite with a PEEK matrix may have a continuous-use temperature as high as 250°C.   |
| Polyimide (PI)                   | A polymer produced by reacting an aromatic dianhydride with an aromatic diamine. It is a highly heat-resistant resin $\geq 315^{\circ}\text{C}$ . Similar to a polyamide, differing only in the number of hydrogen molecules contained in the groupings. May be either thermoplastic or thermosetting.  |
| Poly(phenylene)                  | A high carbon content (94.7 percent) polymer that has the monomeric repeat unit $-(\text{C}_6\text{H}_4)-$ .  |
| Polyphenylene<br>sulfide (PPS)   | A high-temperature thermoplastic useful primarily as a molding compound. Known for chemical resistance.   |
| Polysulfone                      | A high-temperature resistant thermoplastic polymer with the sulfone linkage, with a $T_g$ of $190^{\circ}\text{C}$ .  |
| Polyvinyl Chloride               | A vinyl-type thermoplastic resin formed by the addition reaction of vinyl chloride monomer.   |
| Rayon                            | A synthetic fiber made up primarily of regenerated cellulose. In the process, cellulose derived from wood pulp, cotton linters, or other vegetable matter   |



is dissolved into a viscose spinning solution. The solution is extruded into an acid-salt coagulating bath and drawn into continuous filaments. Rayon fibers were one of the first precursor materials to be used in the manufacture of carbon fibers. They have now been almost completely replaced by PAN and pitch fibers as starting materials for carbon fiber manufacture due to low yields, high processing costs, and limited physical property formation.

|                           |   |
|---------------------------|---|
| <b>Resin</b>              | A solid or pseudosolid organic material usually of high molecular weight that exhibits a tendency to flow when subjected to stress. Used in reinforced plastics, to bind together the reinforcing material; the matrix.   |
| <b>Resistance furnace</b> | In the carbon fiber process, a carbonization furnace that utilizes resistance heating to eliminate the heteroatoms from the carbon fiber structure. In this furnace, heat distribution is obtained by a combination of direct radiation from the resistors and reradiation from the interior surfaces of the furnace chamber to temperatures in excess of 1000°C. |
| <b>S-glass</b>            | A magnesium aluminosilicate composition that is especially designed to provide very high tensile strength glass filaments.  |
| <b>Sizing</b>             | A coating put on the fiber, usually at the time of manufacture, to protect the surface and aid the process of handling and fabrication or to control the fiber characteristics. Most standard sizes used for aerospace-grade carbon fibers are epoxy based.   |
| <b>Spinnerette</b>        | A metal disc containing numerous minute holes used in yarn extrusion. The spinning solution or molten polymer is forced through the holes to form the yarn filaments.   |
| <b>Stabilization</b>      | In carbon fiber manufacture the process used to render the carbon fiber precursor infusible prior to carbonization.   |
| <b>Surface treatment</b>  | In carbon fiber manufacturing, surface treatment is the process step whereby the surface of the carbon fiber is oxidized in order to promote wettability and adhesion with the matrix resin in the composite.   |
| <b>Tensile strength</b>   | The pulling stress required to break a given specimen.  |

**Thermal oxidative stability**

The resistance of a fiber, resin, or composite material to degradation upon exposure to elevated temperature in an oxidizing atmosphere. It is often measured as percent weight loss after exposure to a specified temperature for a set period of time. It may also be measured as the percentage of retained properties after elevated-temperature exposure.

**Thermoplastic polymers**

Polymers capable of being repeatedly softened by an increase of temperature and hardened by a decrease in temperature. Applicable to those polymers whose change upon heating is substantially physical rather than chemical and that in the softened stage can be shaped by flow into articles by molding or extrusion.

**Thermoset polymers**

Polymers that, when cured by application of heat or chemical means, change into substantially infusible and insoluble materials.

**Toughness**

A property of a material for absorbing work. The actual work per unit volume or unit mass of material that is required to rupture it.

**Tow**

An untwisted bundle of continuous filaments. A tow designated as 12K has 12,000 filaments.

**Whiskers**

Materials characterized by their fibrous, single-crystal structures, which have almost no crystalline defects. Numerous materials, including metals, oxides, carbides, halides, and organic compounds, have been prepared in the form of whiskers. They are often used to reinforce resin- and metallic-matrix composites.

## APPENDIX

### Biographical Sketches of Committee Members

RUSSELL J. DIEFENDORF received a BS from the University of Rochester and a PhD in physical chemistry from the University of Toronto. Prior to accepting the position of Professor in the Chemical Engineering Department at Clemson University, he was Professor of Materials Sciences at Rensselaer Polytechnic Institute. He was previously at General Electric where he held positions in the Missile and Ordnance Department and the Research Laboratory. His research interests include mechanical properties; structure to properties; graphite; pyrolytic materials; boron and carbon fibers; composite structures and materials; high temperature composites; and gas phase kinetics.

CHARLES P. BEETZ, JR. received his BS in physics and mathematics from Morehead State University and a MS and PhD in Physics at Purdue University. Prior to his present position of Director of Thin Film Research and Development, at Advanced Technology Materials, Inc., he held positions at General Motors Research Laboratory and American Cyanamid Company. He is active in several professional societies and was Technical Area Chairman of the SAMPE 17th Biennial Carbon Conference and Session Chairman of Gordon Conference on Composites.

GENE P. DAUMIT received his BS in chemistry from the University of Maryland and his PhD in organic chemistry from the Massachusetts Institute of Technology. He is the Technical Director of Celion® Carbon Fibers, BASF Structural Materials, Inc., and has previous experience with Fiber Industries and Celanese. Since 1978 he has been involved in the composites industry; in his current position, he has overall responsibility for all carbon fiber research including precursor development, new carbon fiber products and manufacturing technology, and new product applications research.

DANNY D. EDIE received his BS (chemical engineering) from Ohio State, a MS (applied mathematics) at the University of Toledo, and his PhD in chemical engineering from the University of Virginia. He worked as a testing and operations engineer at NASA's Lewis Research Center in Cleveland and a senior research engineer at Celanese Corp. Research and Development Division before

accepting the position of Assistant Professor of Chemical Engineering at Clemson University. Since 1982 he has been Professor of Chemical Engineering and is also Co-Director of the Advanced Engineering Fibers Laboratory.

MICHAEL JAFFE received his BA from Cornell University and his PhD in Chemistry from Rensselaer Polytechnic Institute. Since 1967 he has been employed by Hoechst Celanese Corporation--as research chemist; senior research chemist; research associate; research supervisor, group leader. He is currently Senior Research Associate. His research interests include morphology of crystalline high polymers; transition behavior of polymers; structure-property relationships of polymers and related materials.

ARTHUR JAMES received his BS degree from Polytechnic Institute of New York. He began work for Lockheed in 1978 as Department Engineer for Advanced Structures Technology Department. From 1984-85 he was Composites Program Manager, and from 1985-87 he worked in Lockheed's Composites Development Center. He is Program Manager in its Contracts R&D Program. His interests include composites technology, especially for application to current and future aircraft; advanced structural and materials technology, including metallic, graphite\epoxy composites and metal matrix composites applications.

RUEY LIN received his BS degree at National Taiwan University and his MS and PhD degrees at West Virginia University. He held previous positions with Carborundum Company, American Kynol, Inc., Stauffer Chemical Company and is a Principal Research Scientist at Howmedica in Rutherford, New Jersey. His research interests are in preparation and characterization of refractory fibers, development of engineering thermoplastics and advanced composite materials for orthopedic applications.

MANUEL PANAR received his PhD in physical organic chemistry at California Institute of Technology in 1960. He has been with Du Pont Central Research and Development Department since 1964. He was Research manager of polymer physics from 1969-85 and in polymer chemistry from 1985-89. His research interests include anisotropic polymer solutions, aramid fiber morphology. He is currently Director of Analytical and Information Sciences.

KARL PREWO is Manager of Materials Sciences at United Technologies Research Center. In this position, he directs the research of a group of scientists who work in the areas of ceramics, metals and metal matrix, and ceramic matrix composites. Dr. Prewo has 20 years of industrial research experience and has authored many articles in the area of fiber reinforced metals and ceramics. He is recipient of United Technologies' highest award for engineering achievement, the George Mead Medal, the Medal of Excellence in Composite Materials from the University of Delaware Center for Composite Materials, and he is a Fellow of ASM.

THEODORE SCHOENBERG received his BChE from City College of New York and his SM and ScD degree in Chemical Engineering from the Massachusetts Institute of Technology. He has worked at TEXTRON Specialty Materials since 1965 and is the Director of Advanced Fiber Development. He has been involved in all aspects of fiber activity during his employment including development of CVD boron fiber to a production stage, large tow carbon fibers, development of SiC

fiber, and most recently, effort on  $\text{TiB}^2$  fibers.

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